Summary

Ovalbumin was hydrolysed with Pronase-P, and the carbohydrate-containing fragments were isolated as two glycopeptides. From partial hydrolysate of glycopeptides in 2*N* hydrochloric acid, N-acetylglucosamine-asparagine compound was isolated in pure, crystalline state, and its structure was established for N-(L-*β*-aspartyl)-2-acetamido-2-deoxy-*β*-D-glucosylamine.

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138. Yoshio Hamashima, Kazuo Tori, and Akira Takamizawa : Camphane Derivatives. VII.*1 Syntheses and Structure of 3-Methyl-3*aβ*, 7*aβ*-bornano[3,2-*d*]oxazolidin-2-one and its Derivatives.

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In the previous paper[1] the reaction of 3*α*-methylaminocamphor (I) with phosgene was reported to give two products, Ⅲ and Ⅳ, besides the main product N-methyl-3-camphorcarbamoyl chloride (Ⅱ). When the reaction mixture was left for a few days, Ⅱ could not be isolated, but Ⅲ was obtained as colorless needles, m.p. 82°, together with a small amount of Ⅳ. In the latter case, the product initially formed seems to be Ⅱ which is subsequently converted into Ⅲ by hydrochloric acid produced during the reaction. Actually, Ⅱ was converted into Ⅲ on gentle warming for a while in methanolic hydrochloric acid or in thionyl chloride.

The compound (Ⅲ), $C_{12}H_{18}O_2NCl$, is an isomer of Ⅱ. Since, in contrast to Ⅱ, Ⅲ does not react readily with amines, the character of the chlorine atom in Ⅲ is not of a carbamoyl chloride type. While the optical rotatory dispersion (ORD) spectrum of Ⅱ exhibits a positive Cotton effect, Ⅲ gives only a negative plain curve, although a strong carbonyl band at 1760 cm^{-1} still appears in the infrared spectrum of Ⅲ. The proton magnetic resonance (NMR) spectrum of Ⅲ shows a slightly doubling doublet at 5.74 τ (J=4.2 and 1.0 c.p.s.) due to the proton on the nitrogen- or oxygen-bearing carbon atom and a triplet-like signal at 7.12 τ ascribable to the proton on the bridgehead C-4 in a bornane skeleton. This implies that the proton giving the doublet is attached at the C-3 position and has an *exo* configuration (*exo* C-3). If this proton is postulated to be either *endo* C-3, *exo* C-2, or *endo* C-2, its signal should appear as a broad singlet, a sharp doublet, or a sharp singlet, respectively.[2~5] Thus Ⅲ may be formulated as a bornane derivative *cis*-fused with an oxazolidinone ring, that is, 3-methyl-7*a*-chloro-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one. The *cis* ring juncture is probably preferable

*1 Part Ⅵ. T. Takahashi, H. Fujimura, Y. Hamashima : Yakugaku Zasshi, 84, 918 (1964).
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1) T. Takahashi, H. Fujimura, Y. Hamashima : Yakugaku Zasshi, 84, 579 (1964).
2) W. D. Kumler, J. N. Shoolery, F. V. Brutcher, Jr. : J. Am. Chem. Soc., 80, 2533 (1958); see also, J. D. Connolly, R. McCrindle : Chem. & Ind. (London), 1965, 379.
3) F. A. L. Anet : Can. J. Chem., 39, 789 (1961).
4) T. J. Flautt, W. F. Erman : J. Am. Chem. Soc., 85, 3212 (1963).
5) For a review, see S. Sternbell : Rev. Pure and Appl. Chem., 14, 15 (1964).

in this case because the *trans*-fusion of this ring system cannot be made without very high ring-strain. This assumption will be confirmed later. On lactonization, some of γ-keto acids and γ-keto acid chlorides, for example, dihydropenicillic acid[6] and levulinyl chloride,[7] are known to be converted into the hydroxylactone and chlorolactone, respectively. Therefore, II regarded as a γ-keto carbamoyl chloride, can reasonably be expected to give the chloro-oxazolidin-2-one by cyclization.

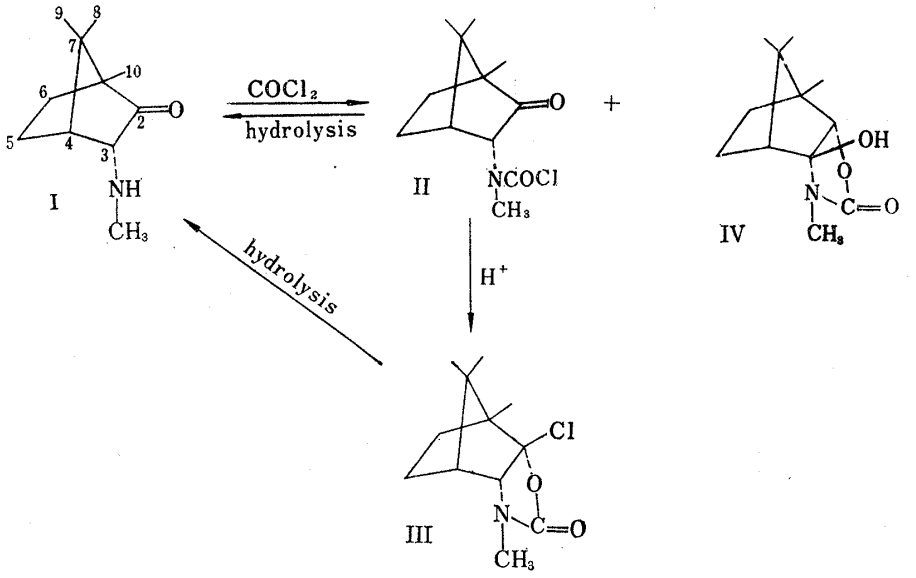


Chart 1.

On acid hydrolysis, III was decomposed to the starting material (I). Heating of III with potassium hydroxide in methanol gave methyl N-methyl-3-camphorcarbamate (VII), which was identified by comparison with an authentic specimen prepared by the reaction of I with methyl chloroformate. These findings provide further evidence for the fact that the chlorine atom in III is situated at the C-7*a*-position of the ring system. Treatment of III with either strong acid or alkali led to the cleavage of the oxazolidinone ring, but under fairly mild conditions, III underwent displacement of the chlorine atom. Thus treatment of III with either methanolic silver nitrate in pyridine or methanolic hydrochloric acid afforded a 7*a*-methoxy derivative (VIII), whereas the use of ethanolic hydrochloric acid led to a 7*a*-ethoxy derivative (IX). On treatment with silver acetate and silver benzoate in pyridine, III was converted into a 7*a*-acetoxy- and a 7*a*-benzoyloxy derivative (X and XI), respectively. The infrared spectrum of VIII shows a strong but broad carbonyl band at 1743 cm^{-1} arising from the cyclic urethan structure, and its ORD curve indicates no Cotton effect. Accordingly, VIII is thought to have the same ring system as III. The NMR spectrum of VIII also supports the above structural assignment. The *endo*-8-methyl signal appears at a relatively high field (9.03 τ) as in the case of X (9.01 τ) (*vide infra*). Since the compounds (IX, X, and XI) have the chemical and physical properties similar to those of VIII, they are also assumed to have the same ring structure.

On catalytic hydrogenation with either palladized charcoal or Raney nickel, III afforded V, $C_{12}H_{19}O_2N$, corresponding to a dechlorinated product of III, in good yield. The infrared spectrum of V shows an intense carbonyl band at 1732 cm^{-1}, but since it gives a positive plain ORD curve, V is also expected to have a tricyclic structure.

6) R. A. Raphael: J. Chem. Soc., **1947**, 805.
7) J. Cason, E. J. Reist: J. Org. Chem., **23**, 1492 (1958).

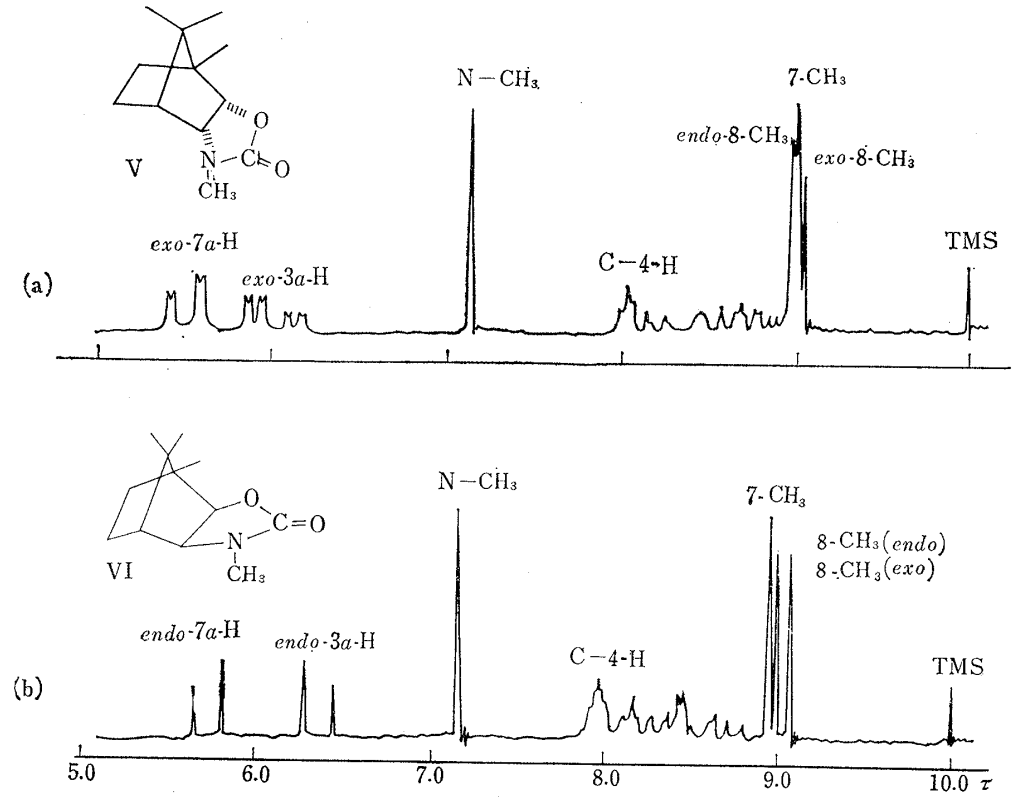


Fig. 1. The Nuclear Magnetic Resonance Spectra of V and VI in Deuteriochloroform

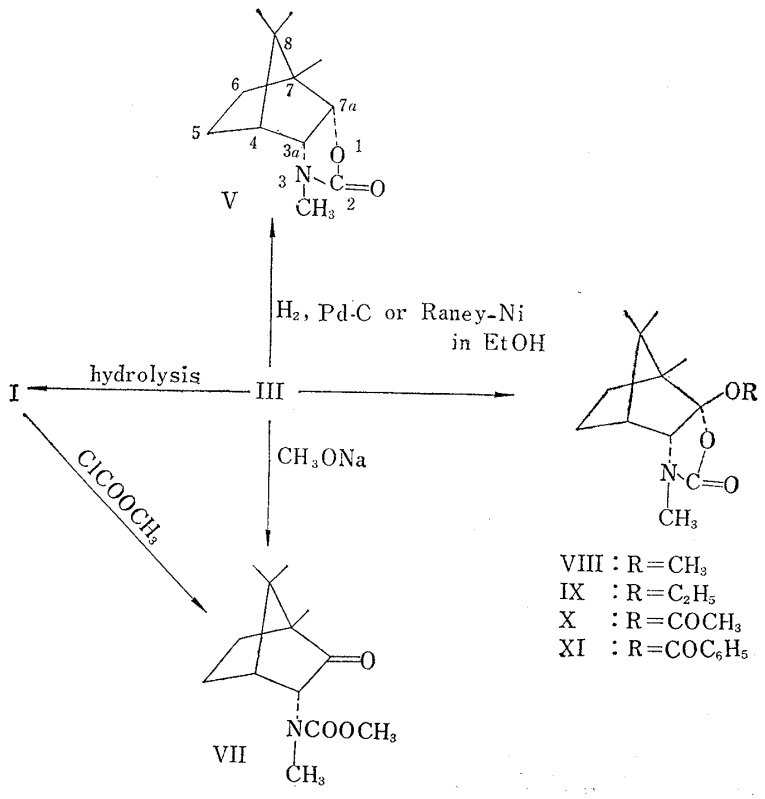


Chart 2.

The NMR spectrum of V, as shown in Fig. 1(a), provides confirmatory evidence that the bornane and oxazolidinone rings are *cis*-fused at the C-3*a*- and C-7*a*-positions and both hydrogens attached to these carbons are *exo*-oriented. The signal of the C-7*a*-proton appears at 5.53 τ as a slightly doubling doublet due to the splittings by the C-3*a*-proton (J=10.0 c.p.s.) and the *exo*-C-6-proton (long-range spin coupling, J=1.2 c.p.s.). The signal of the C-3*a*-proton at 5.96 τ is split into a slightly doubling quartet by the C-7*a*-proton (J=10.0 c.p.s.), the bridgehead C-4-proton (J=4.0 c.p.s.), and the *exo*-C-5-proton (long-range coupling, J=1.2 c.p.s.). These coupling constants[2~5] are quite consistent with the assumed structure of V, namely, 3-methyl-3*a*β,7*a*β-bornano[3,2-*d*]-oxazolidin-2-one, and this structure was confirmed by synthesis.

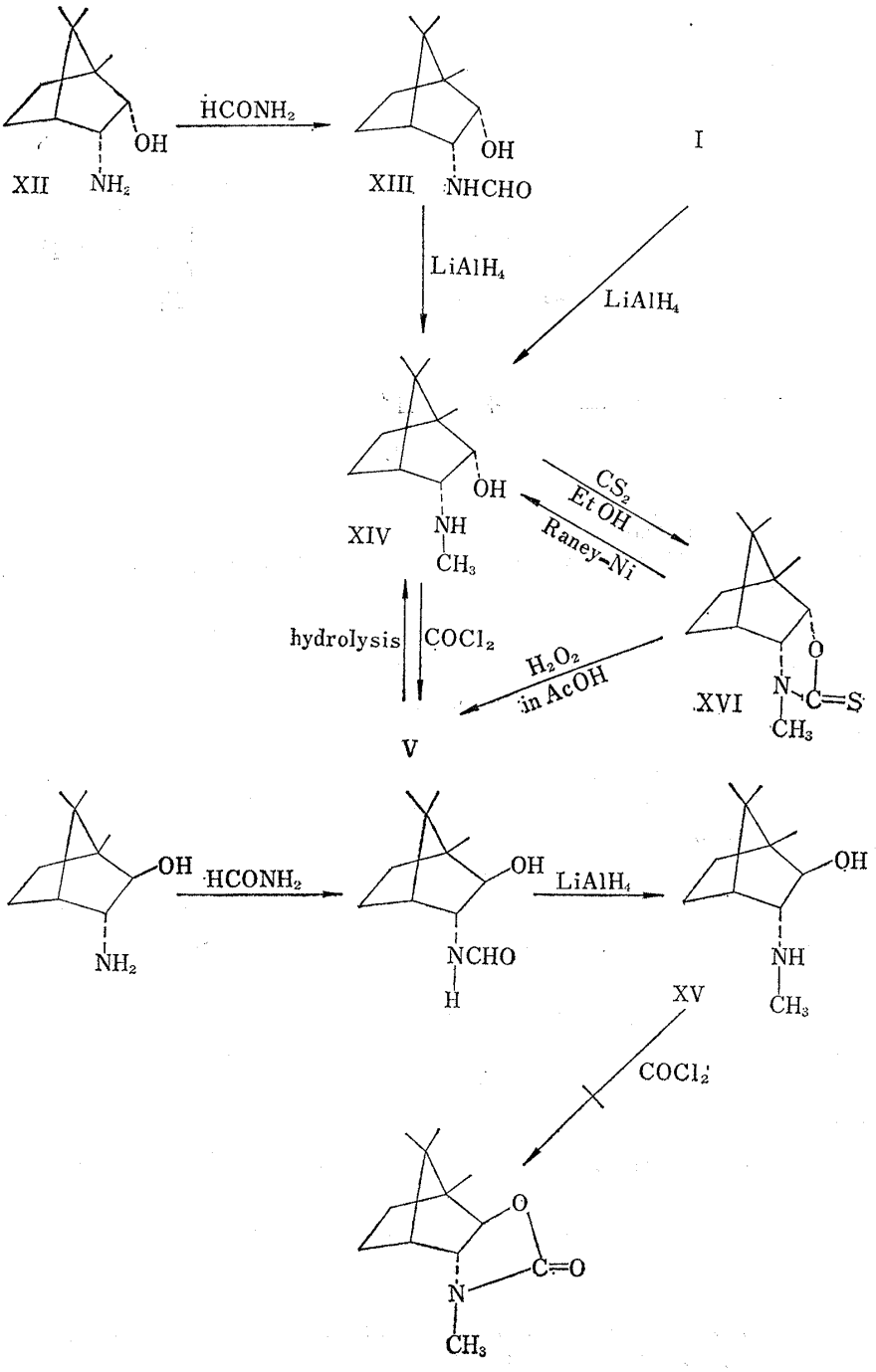


Chart 3.

3α-Aminoborneol (XII),[8] on treatment with formic acid, followed by reduction with lithium aluminum hydride, gave 3α-methylaminoborneol (XIV),[1,9] which was converted into V by the action of phosgene in fairly good yield. In contrast to XIV, 3α-methylaminoisoborneol (XV)[9] derived from 3α-aminoisoborneol[8] in a similar manner did not undergo cyclization. Acid or alkaline hydrolysis of V gave back XIV. Accordingly, it seems that the configuration of XIV was retained during the cyclization reaction. In accordance with Kitamura's method,[10] XIV was treated with carbon disulfide in methanol to furnish 3-methyl-3$a\beta$,7$a\beta$-bornano[3,2-d]oxazolidin-2-thione (XVI), which was converted into V on oxidative desulfurization with hydrogen peroxide in acetic acid. Thus the structure of V, and accordingly those of III, VIII, IX, X, and XI were confirmed unambiguously.

Chart 4 explains the mechanism for the formation of III.

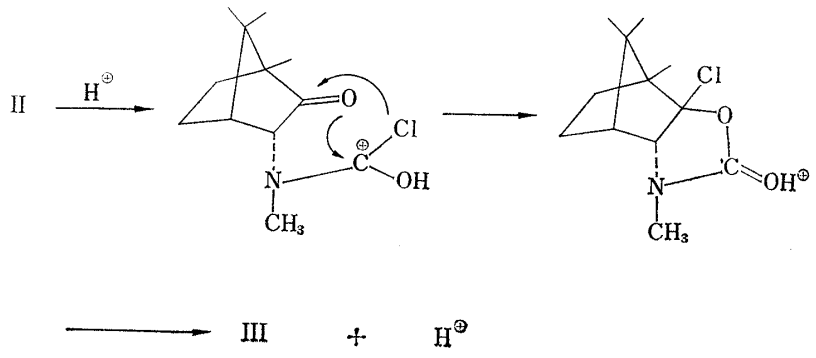


Chart 4.

The compound (IV), $C_{12}H_{19}O_3N$, m.p. 193°, shows a strong carbonyl band at 1736 cm^{-1} and a hydroxyl band at 3260 cm^{-1} in the infrared spectrum, but it gives a positive ORD curve. These findings suggest that IV also has a bornano[3,2-d]oxazolidin-2-one ring system containing a hydroxyl group, instead of the chlorine atom, as experienced in III. In the NMR spectrum of IV, the signal of the proton on the nitrogen- or oxygen-bearing carbon atom appears at 5.54 τ as a sharp doublet (long-range spin coupling, J=1.0 c.p.s.), and a broad doublet signal at 8.01 τ is due to the bridgehead C-4-proton. Furthermore, a sharp singlet signal of a hydroxyl group was clearly detected. These facts imply that the hydroxyl group is substituted at the C-3-position and the C-2-proton is *exo*-oriented.[2~5] Acetylation of IV with acetic anhydride-pyridine gave the acetate (XVII), which was considered as an isomer of X. However, on acid hydrolysis, XVII underwent deacetylation to give the compound (IV), whereas X was decomposed to I under the same conditions. In comparison of the ORD spectrum of X with that of XVII, the former shows a positive plain curve and the latter a negative one. This fact also suggests that these compounds are isomers differing only in the substituted position of the angular acetoxyl group. Thus IV can be formulated as 3-methyl-3a-hydroxy-3$a\beta$,7$a\beta$-bornano[3,2-d]oxazolidin-2-one.

Chlorination of IV by thionyl chloride or phosphorus pentachloride produced an unexpected product (XVIII), $C_{12}H_{17}O_2NCl_2$, m.p. 132°, which shows a negative plain ORD curve. Its infrared spectrum shows an intense carbonyl band at 1780 cm^{-1} which is shifted to relatively higher frequencies as compared with that exhibited by the carbonyl group in IV. These facts indicate that two chlorine atoms in XVIII are substituted

8) E. E. van Tamelen, W. F. Tousignant, P. E. Peckham : J. Am. Chem. Soc., **75**, 1297 (1953).
9) K. Tori, Y. Hamashima, A. Takamizawa : This Bulletin, **12**, 924 (1964).
10) R. Kitamura : Yakugaku Zasshi, **54**, 1 (1934).

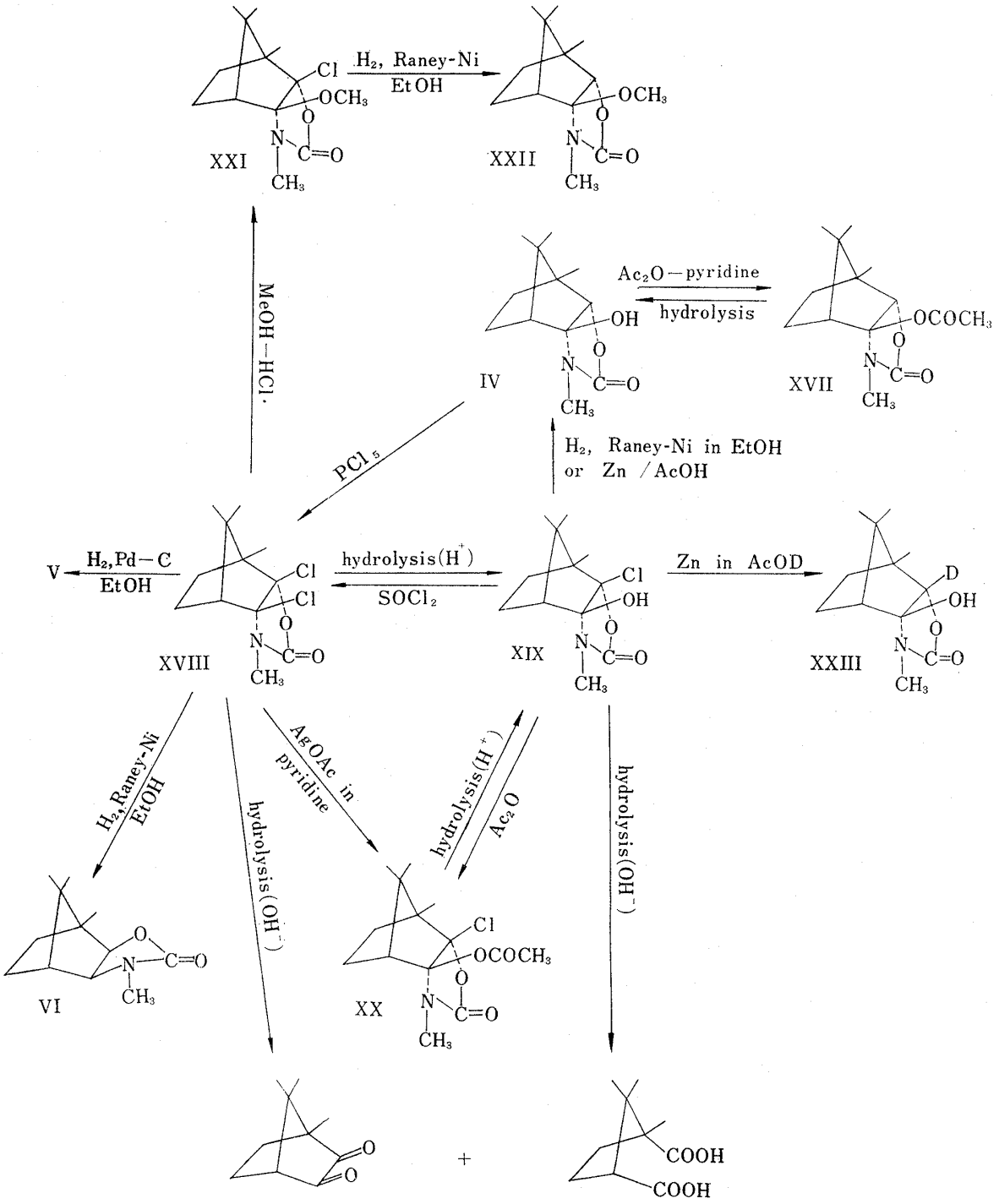


Chart 5.

at the C-3*a*- and C-7*a*-positions, where they can exert a significant effect on the carbonyl group of the oxazolidinone ring. Furthermore, the NMR spectrum of XVIII shows no peak corresponding to protons on the nitrogen- or the oxygen-bearing carbon atom, except for the N-methyl group, but a signal of the bridgehead C-4-proton is observed at 7.50 τ as a fairly clear doublet. Thus XVIII can be formulated as 3-methyl-3*a*,7*a*-dichloro-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one.

Acid hydrolysis of XVIII gave the product (XIX) corresponding to the monohydroxylated compound, $C_{12}H_{17}O_2NClOH$, which was fairly stable against acids, but, upon

treatment with methanolic potassium hydroxide, was decomposed to camphorquinone[11] and partly to *d*-camphoric acid.[12] Camphorquinone was also derived from XVIII by either Raney nickel or zinc-acetic acid afforded IV quantitatively. These results confirmed the hydroxyl group or the chlorine atom in IV, XVIII, and XIX to be situated at the C-3*a*- or the C-7*a*-position. Reaction of XVIII with silver acetate-pyridine or acetylation of XIX with acetic anhydride-pyridine gave the acetate (XX), which on acid hydrolysis let to XIX. XVIII, on treatment with either silver nitrate-pyridine in methanol or methanolic hydrochloric acid, afforded a methoxy derivative (XXI). Subsequent hydrogenation of XXI with Raney nickel produced the dechlorinated compound (XXII), which is an isomer of VII. Dechlorination of XIX was also effected by zinc-deuteriated acetic acid, whereby XXIII, $C_{12}H_{18}O_3ND$, m.p. 193°, a monodeuteriated derivative of IV, was obtained, the NMR spectrum of which was identical with that of IV except for the absence of the C-7*a*-proton signal at 5.54 τ. Thus the structures of XIX, XX, XXI, XXII, and XXIII can be pictured as shown in Chart 5.

The product derived from XVIII by hydrogenation with palladium-charcoal in alkaline methanol was identified as V. On the other hand, hydrogenation of XVIII with Raney nickel afforded VI, as colorless thin plates, m.p. 123°, which was an isomer of V. The ORD curve of VI shows a plain curve whose sign is opposite to that of V. A sharp AB-type quartet (5.74 ane 6.37 τ; J=8.0 c.p.s.) in the NMR spectrum of VI, as shown in Fig. 1(b), evidently indicates that the C-3*a*- and the C-7*a*-protons are *endo*-oriented to the bornane skeleton, and accordingly the assumed oxazolidinone ring has an *exo*-configuration. Furthermore, the signal of the C-4-proton appears at 8.00 τ as a multiplet, which is consistent[3] with the structure of 3-methyl-3*a*α,7*a*α-bornano[3,2-*d*]oxazolidin-2-one.

The methyl signals in the NMR spectra of the derivatives of V which we synthesized can serve to confirm the structures assigned above. In the previous paper,[9] we have reported from an NMR study of many bornane derivatives that the 10-methyl*[3] signal has a greater amplitude than the other two angular methyl signals of an almost equal amplitude, and that the additional shift values of the 8-methyl signal due to a 2-*exo*-hydroxyl, a 2-*exo*-acetoxyl, a 2-*exo*-chlorine, and a 2-*exo*- or a 3-*exo*-bromine are about −0.20, −0.16, −0.27, and −0.31 p.p.m., respectively. Furthermore, the additivity of additional shift values due to substituents was also found to be valid for the bornane skeleton.[9] Such additivity rule is well established in the NMR spectra of steroids.[13] Thus we assigned signals given by a series of derivatives of V as shown in Table I, in which we also list the values of displacement of the signal positions for the methyl groups and the bridgehead C-4-proton from those of V which was taken as a reference compound. Apparently, in this ring system, the additivity rule is also held. Particularly, in the *endo*-8-methyl signal the additional shift value due to *exo*-substituents was observed to be strictly additive, except for the case of XIX, and the additional shift values due to an *exo*-hydroxyl, an *exo*-acetoxyl, and an *exo*-chlorine are taken to be −0.20, −0.05, and −0.20 p.p.m., respectively. These values, in comparison with those obtained from the bornane system as mentioned above, are somewhat smaller particularly when the substituent is an acetoxyl. The cause of this appreciable difference may be referred by the presence of the oxazolidinone ring attached to the C-2 and C-3 atoms of the bornane system. The smaller additional shift value for the *endo*-8-methyl signal in XIX is probably due to a mutual interaction

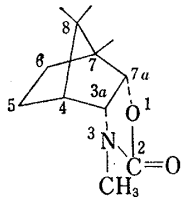
*3 Since this numbering system is based on the bornane skeleton, this methyl group corresponds to the 7-methyl of bornano[3,2-*d*]oxazolidin-2-one system.

11) H. Rupe, A. T. di Vignano : Helv. Chim. Acta, **20**, 1078 (1937).

12) W. Hartmann : Ber., **21**, 222 (1888).

13) For example, see R. F. Zürcher : Helv. Chim. Acta, **46**, 2054 (1963).

TABLE I. Nuclear Magnetic Resonance Data on 3-Methyl-3aβ,7aβ-bornano[3,2-*d*]oxazolidin-2-one (V) and its Related Compounds[a)]



Compound	Chemical shift (τ)						
	7-CH_3	*exo*-8-CH_3	*endo*-8-CH_3	N-CH_3	4-H	3*a*-H	7*a*-H
V[c)]	9.04	9.07	9.03	7.20	8.03[t]	5.96[o]	5.53[q]
IV	9.03	9.05	8.83	7.21	8.01[d]	—	5.54[d]
	(−0.01)	(−0.02)	(−0.20)	(+0.01)	(−0.01)		
XVII	9.01	9.01	8.98	7.26	7.77[d]	—	5.25[d]
	(−0.03)	(−0.06)	(−0.05)	(+0.06)	(−0.26)		
VIII	9.03	9.10	9.03	7.17	7.97[t]	6.10[q]	—
	(−0.01)	(+0.03)	(0.00)	(−0.03)	(−0.06)		
X	9.01	9.01	9.01	7.16	7.95[t]	5.85[q]	—
	(−0.03)	(−0.06)	(−0.02)	(−0.04)	(−0.08)		
III	8.90	8.98	8.83	7.12	7.89[t]	5.74[q]	—
	(−0.14)	(−0.09)	(−0.20)	(−0.08)	(−0.14)		
XXIII	9.03	9.05	8.82	7.22	8.01[d]	—	—
	(−0.01)	(−0.02)	(−0.21)	(+0.02)	(−0.02)		
XIX[b)]	8.85	8.99	8.72	7.12	7.81[d]	—	—
	(−0.19)	(−0.08)	(−0.31)	(−0.08)	(−0.22)		
XX	8.87	8.99	8.77	7.16	7.44[d]	—	—
	(−0.17)	(−0.08)	(−0.26)	(−0.04)	(−0.59)		
XVIII	8.84	8.97	8.61	7.07	7.50[d]		
	(−0.20)	(−0.10)	(−0.42)	(−0.13)	(−0.53)		
VI[c)]	8.97	9.09 or 9.03	9.03 or 9.09	7.16	8.00[m]	6.37[d]	5.74[d]

a) Observed on about 10% (w/v) solutions in deuteriochloform. Multiplicities of signals are represented as d (doublet), t (triplet), q (quartet), o (octet), and m (multiplet). Values in parentheses are displacement of the signal positions from those of V which is taken as a reference compound. Plus sign represents an upfield shift.
b) Observed on a saturated solution.
c) Reported and discussed in ref. 9.

between the chlorine and the hydroxyl group, which are capable of making a hydrogen-bonding in this situation.[14)] Since if the ring system of V should vary from compound to compound, no such simple additivity would be observed for the signal shifts due to the substituents, as shown in Table I, the above NMR spectral evidence also confirms the assignment of the configurations of all the compounds listed to be correct. Further work on the reaction mechanisms for the formation of IV from I and of XVIII from IV is in progress.

Experimental[*4]

Chlorocarbonylation of 3α-Methylaminocamphor (I) with Phosgene——Excess of phosgene in benzene

[*4] The NMR spectra were taken with a Varian A-60 spectrometer, the calibration of which was checked according to Tiers and Hotchkiss,[15)] on about 10% (w/v) solutions in deuteriochloroform containing tetramethylsilane as an internal reference at room temperature. Accuracies of the measurements are about ±0.02 τ for chemical shifts and about ±0.3 c.p.s. for coupling constants. The ORD curves were measured on a Rudolf automatically recording spectropolarimeter at room temperature. All melting points are uncorrected.

14) C. M. Huggins, G. C. Pimentel, J. N. Shoolery : J. Phys. Chem., **60**, 1311 (1956).
15) G. V. D. Tiers, D. R. Hotchkiss : *Ibid.*, **66**, 560 (1962).

was added dropwise under stirring to a boiling suspension of powdered 3α-methylaminocamphor hydrochloride (10 g.) in dry benzene until the suspension became clear. The solution was concentrated to dryness to give 9.5 g. of a resinous oily residue. This oily residue was taken up in benzene and the organic layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on alumina, and elution with ether gave the product (7 g.) which was recrystallized from ether-hexane to give N-methyl-3-camphorcarbamoyl chloride (II) as cololrless needles, m.p. 82°. $[\alpha]_D^{25}$ +142°($CHCl_3$). ORD in MeOH (c=1.048): $[\alpha]_{700}$ +54°, $[\alpha]_{600}$ +72°, $[\alpha]_{500}$ +124°, $[\alpha]_{400}$ +256°, $[\alpha]_{350}$ +575°, $[\alpha]_{300}$ −150°. IR ν_{max}^{Nujol} cm^{-1}: 1745 (C=O), 1730 (C=O), and 1044 (C-O). *Anal.* Calcd. for $C_{12}H_{18}O_2NCl$: C, 59.13; H, 7.44; N, 5.75. Found: C, 59.28; H, 7.54; N, 5.67.

The product (0.36 g.) eluted with MeOH was recrystallized from MeOH-ether to give IV as colorless sticks, m.p. 193°. $[\alpha]_D^{25}$ +127.7°($CHCl_3$). ORD in MeOH (c=0.542): $[\alpha]_{700}$ +86°, $[\alpha]_{600}$ +112°, $[\alpha]_{500}$ +182°, $[\alpha]_{400}$ +328°, $[\alpha]_{300}$ +670°. IR ν_{max}^{Nujol} cm^{-1}: 3260 (OH), 1738 (C=O), 1087, 1048 (C-O), and 1003 (OH). *Anal.* Calcd. for $C_{12}H_{19}O_3N$: C, 63.97; H, 8.50; N, 6.22. Found: C, 63.83; H 8.62; N, 6.17. Further elution with methanol yielded 3α-methyl aminocamphor (I) hydrochloride (0.3 g.).

The resinous oil obtained by concentration of the reaction mixture described above was redissolved in benzene and the organic layer was washed with 10% Na_2CO_3 and then with water and dried over anhydrous $MgSO_4$ for some time. Removal of the solvent left an oily residue which solidified within several days with evolution of hydrogen chloride. The ether-soluble fraction of the solids was washed with dil. aqueous Na_2CO_3 and was submitted to alumina (neutral) chromatography. A fraction eluted with ether was evaporated and the product was recrystallized from ether-hexane to give 3-methyl-7*a*-chloro-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (III) as colorless needles, m.p. 82°. Yield, 5 g. $[\alpha]_D^{25}$−22° ($CHCl_3$). ORD in MeOH (c=1.006): $[\alpha]_{700}$ −15°, $[\alpha]_{600}$ −16°, $[\alpha]_{500}$ −23°, $[\alpha]_{400}$ −70°, $[\alpha]_{300}$ −275°, $[\alpha]_{250}$−900°. IR ν_{max}^{Nujol} cm^{-1}: 1760 (C=O), 1027, and 1016 (C-O). *Anal.* Calcd. for $C_{12}H_{18}O_2NCl$: C, 59.13; H, 7.44; N, 5.75. Found: C, 59.22; H, 7.49; N, 5.72. The product eluted with MeOH and the ether-insoluble crystals (described above) were combined and recrystallized from MeOH to furnish an additional amount (0.40 g.) of IV.

Isomerisation of II with Acid——a) II (0.2 g.) was refluxed with 5 ml. of 25% HCl-MeOH for 2 hr. After removal of the solvent under reduced pressure, the residue was extracted with ether and the oraganic layer was washed with water, then cold 10% aqueous NaOH, and dried over anhydrous $MgSO_4$. The filtered solution was concentrated and chromatographed on alumina. Colorless needles, m.p. 82°, were obtained from the first eluate fraction with ether, which were identified as 3-methyl-7*a*-chloro-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (III) by mixture melting point determination and comparison of the IR spectra. Yield, 0.092 g. The second ether eluate fraction yielded colorless rocks, m.p. 122°, which were identical with 3-methyl-7*a*-methoxy-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (VIII), described later. Yield, 0.046 g.

b) II (0.5 g.) was heated under reflux with 3 ml. of $SOCl_2$ for 5 hr., and the solution was evaporated *in vacuo* and extracted with benzene. The benzene extract was washed with 5% aqueous NaOH, dried (K_2CO_3), and evaporated, leaving a crystalline residue. Chromatography of the residue on alumina (neutral) in ether afforded 0.35 g. of colorless needles (III), m.p. 82°.

Hydrolysis of III with Hydrochloric Acid——A suspension of 20 mg. of III in 4 ml. of 20% HCl was heated on a steam bath at 80° for 30 min. until gas evolution (carbon dioxide) had ceased. After concentration of the solution to dryess, the residue (15 mg.) was crystallized to give a colorless 3α-methylaminocamphor (I) hydrochloride, m.p. 238°(decomp.), which was identified by direct comparison with an authentic specimen.

Methyl N-Methyl-3-camphorcarbamate (VII)——a) To an ethereal solution containing 2 mol. of I was added dropwise under ice-cooling and stirring 1 mol. of methyl chloroformate. After being stirred at room temperature for 1 hr., the reaction mixture was filtered and washed. The filtrate and the washings were concentrated to give colorless oil (VII), $b.p_1$ 130~140°, which gradually solidified to colorless plates, m.p. 53~54°. IR ν_{max}^{Nujol} cm^{-1}: 1744, 1696, and 1162. *Anal.* Calcd. for $C_{13}H_{21}O_3N$: C, 65.24; H, 8.85; N, 5.85. Found: C, 65.19; H, 8.79; N, 6.11.

b) A mixture of III (100 mg.) and KOH (200 mg.) in MeOH (10 ml.) was refluxed for 10 hr., and was worked up in the usual manner to give colorless oil, $b.p_1$ 135°, m.p. 50°, which was identified as VII by direct comparison of their IR spectra.

c) A solution of III (480 mg.) in 5 ml. of MeOH containing 500 mg. of Na was warmed at 70° for 30 min., filtered, and the filtrate was concentrated *in vacuo*, extracted with ether, and the organic layer was washed with water and dried ($MgSO_4$). Removal of the solvent left colorless oil, $b.p_1$ 130~140°, which was identified as VII by IR spectra comparison. Yield, 400 mg.

3-Methyl-7*a*-methoxy-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (VIII)——a) A mixture of 1 g. of III and 15 ml. of 30% methanolic hydrogen chloride was refluxed for 10 hr., concentrated *in vacuo* and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with H_2O, dried over anhydrous K_2CO_3, and evaporated. Recrystallization of the product gave VIII as colorless scales, m.p. 122°. Yield, 0.6 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2817 (CH_3O), 1740 (C=O), 1260, and 1030 (C-O). ORD in MeOH (c=0.539): $[\alpha]_{700}$ +9°,

$[\alpha]_{600}$ +22°, $[\alpha]_{500}$ +33°, $[\alpha]_{400}$ +37.5°, $[\alpha]_{300}$ +39°, $[\alpha]_{250}$ 0°. *Anal.* Calcd. for $C_{13}H_{21}O_3N$: C, 65.24; H, 8.85; N, 5.85; CH_3O, 12.97. Found: C, 65.58; H, 9.02; N, 5.72; CH_3O, 13.05.

b) One mole of III was warmed with methanolic silver nitrate (1.2 mol.) in pyridine at 70° for 2 hr., and the reaction mixture was treated by the ordinary method to give colorless scales, m.p. 122° undepressed by admixture with the sample obtained in a). They also gave identical IR spectra.

3-Methyl-7*α*-ethoxy-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (IX)——One gram of III was treated with 25% HCl in EtOH according to the procedure described for the methoxy isomer (VIII). $b.p_{0.07}$ 145°, light yellow oil (0.9 g.). *Anal.* Calcd. for $C_{14}H_{23}O_3N$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.17; H, 9.37; N, 5.41.

Acid Hydrolysis of VIII and IX——Both VIII and IX were easily hydrolyzed to I on treatment with conc. HCl.

3-Methyl-7*α*-acetoxy-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (X)——A mixture of 2.44 g. of III and 2.00 g. of silver acetate in HOAc was refluxed for 8 hr., cooled, and filtered. The filtrate and the washings were concentrated to dryness, extracted with benzene, and the organic layer was washed with dil. aqueous ammonia and then with H_2O, dried ($MgSO_4$), and evaporated. Recrystallization of the product from hexane gave X as colorless rhombs, m.p. 107° (2.1 g.). ORD in MeOH (c=0.984): $[\alpha]_{700}$ −30.5°, $[\alpha]_{600}$ −41°, $[\alpha]_{500}$ −72°, $[\alpha]_{400}$ −120°, $[\alpha]_{300}$ −316°. IR ν_{max}^{Nujol} cm^{-1}: 1770, 1758, 1259, 1230, 1085, and 1021. *Anal.* Calcd. for $C_{14}H_{21}O_4N$: C, 62.90; H, 7.92. Found: C, 62.99; H, 8.21.

3-Methyl-7*α*-benzoyloxy-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (XI)——III (240 mg.) was mixed well with 230 mg. of silver benzoate and 2 g. of benzoic acid. The mixture was allowed to melt by heating at 150~160° for 10 hr. After cooling, the reaction mass was extracted with benzene, and the organic layer was washed thoroughly with 5% aq. Na_2CO_3, dried ($MgSO_4$), and evaporated. The residue, after recrystallization from acetone-hexane gave XI as colorless plates, m.p. 153~154°. Yield, 200 mg. $[\alpha]_D^{23}$ −47.2° ($CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 1762 (C=O), 1734 (C=O), 1600 (C=C), 1279, and 1095 (C-O). *Anal.* Calcd. for $C_{19}H_{23}O_4N$: C, 69.28; H, 7.04. Found: C, 69.10; H, 7.26.

Hydrolysis of X and XI——The acid hydrolysis of both X and XI led to I, giving no other products or intermediates.

Catalytic Hydrogenation of III——To a solution of 100 mg. of III and 200 mg. of KOH in 10 ml. of MeOH was added 100 mg. of 10% palladized charcoal. The mixture was stirred under H_2 at room temperature and atmospheric pressure (uptake of H_2, 9 ml. within 1 hr., theoretical 9.1 ml.). The catalyst was filtered off and the filtrate was neutralized with HCl, concentrated *in vacuo*, and extracted with benzene. The benzene extract was washed successively with aq. NaOH, H_2O, HCl, and H_2O and dried over anhydrous $MgSO_4$. The crystalline residue after removal of the solvent was recrystallized from ether to give V as colorless sticks, m.p. 119°. Yield, 60 mg. $[\alpha]_D^{28}$ +108.2° ($CHCl_3$). ORD in MeOH (c=1.005): $[\alpha]_{700}$ +82°, $[\alpha]_{600}$ +110°, $[\alpha]_{500}$ +160°, $[\alpha]_{400}$ +240°, $[\alpha]_{250}$ +800°. IR ν_{max}^{Nujol} cm^{-1}: 1732, 1252, 1122, and 1031. *Anal.* Calcd. for $C_{12}H_{19}O_2N$: C, 68.86; H, 9.15; N, 6.69. Found: C, 68.69; H, 9.05; N, 6.63. No basic product was detected.

The same hydrogenation product was also obtained by using Raney-Ni in alkaline medium in fairly good yield.

Synthesis of 3-Methyl-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (V). i) 3*α*-Formamidoborneol (XIII)——a) A mixture of 300 mg. of XII and 3 ml. of 98% formic acid was heated at 110° for 6 hr., concentrated, and extracted with $CHCl_3$. The $CHCl_3$ extract was washed successively with H_2O, 5% HCl, 10% aq. NaOH, and water, dried ($MgSO_4$), and evaporated. Recrystallization of the product from ether gave colorless silky needles of m.p. 143°. Yield, 150 mg. *Anal.* Calcd. for $C_{11}H_{19}O_2N$: C, 67.19; H, 9.71. Found: C, 67.20; H, 9.85.

b) A mixture of 100 mg. of XII and 100 mg. of formamide was heated at 120° for 10 min., poured into water, and extracted with $CHCl_3$ to give colorless needles (100 mg.), m.p. 143°. The identity with the sample obtained in a) was established by mixture melting point determination and comparison of the IR spectra.

ii) 3*α*-Methylaminoborneol (XIV)——a) XIII (300 mg.) in tetrahydrofuran was added dropwise under ice-water cooling to $LiAlH_4$ (200 mg.) in tetrahydrofuran. The mixture was refluxed with stirring for 4 hr., and treated by the ordinary method to give XIV as colorless prisms, m.p. 85~86° (hexane). Yield, 200 mg. *Anal.* Calcd. for $C_{11}H_{21}ON$: C, 72.08; H, 11.55. Found: C, 72.00; H, 11.59. Picrate m.p. 217° (EtOH), oxalate m.p. 203~205° (decomp.) (acetone).

b) A solution of 3 g. of I in ether was added to the ethereal solution of $LiAlH_4$ (300 mg.), and the mixture was stirred at room temperature for 2 hr. The excess $LiAlH_4$ was decomposed with 20% aq. NaOH, the organic layer was washed with H_2O, dried oved anhydrous K_2CO_3, and evaporated. Recrystallization of the residue from hexane gave XIV as colorless prisms, m.p. 85° (1.0 g.).

iii) 3-Methyl-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (V)——To a mixture of 500 mg. of XIV, 10 ml. of benzene and 10 ml. of 10% Na_2CO_3 was added under stirring 20% phosgene in benzene until the organic layer became clear. Throughout the reaction the solution was kept alkaline. The organic layer was washed with H_2O, then dil. HCl, and dried over anhydrous $MgSO_4$. Removal of the solvent and crystallization of the residue from ether afforded V as colorless sticks, m.p. 119°. Yield, 510 mg. $[\alpha]_D^{26}$ +108°

($CHCl_3$). *Anal.* Calcd. for $C_{12}H_{19}O_2N$: C, 68.86; H, 9.15. Found : C, 68.69; H, 9.27. This compound was proved to be identical with the product obtained by catalytic hydrogenation of III by mixture melting point determination and IR spectra comparison.

iv) Alkaline Hydrolysis of V——V (10 mg.) was refluxed with MeOH (2 ml.) containing KOH (200 mg.) for 6 hr., concentrated, and extracted with ether, and the organic layer was washed with H_2O and dried. Removal of the solvent gave colorless prisms (6 mg.), m.p. 80~82°, undepressed by admixture with XIV. Direct comparison of their IR spectra also showed them to be identical.

v) 3-Methyl-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidine-2-thione (XVI)——A mixture of XIV (200 mg.) and carbon disulfide (2 ml.) in EtOH (15 ml.) was heated under reflux until no more hydrogen sulfide gas was evolved (15 hr.). During the reaction a further amount of carbon disulfide was added, and the solution was evaporated and extracted with $CHCl_3$. The $CHCl_3$ extract was washed successively with dil. HCl, H_2O, 5% aq. NaOH, and H_2O, dried ($MgSO_4$), and evaporated. Recrystallization of the product from MeOH gave XVI as colorless thin plates, m.p. 206°. Yield, 120 mg. IR ν_{max}^{Nujol} cm^{-1} : 1510. *Anal.* Calcd. for $C_{12}H_{19}ONS$: C, 63.97; H, 8.50; N, 6.21. Found : C, 63.71; H, 8.64; N, 6.03.

vi) Desulfurisation of XVI with Raney Nickel——A suspension of 120 mg. of XVI and 500 mg. of Raney-Ni (W-II) in EtOH (20 ml.) was stirred at room temperature for 3 hr. and left overnight. The catalyst was removed by filtration, and the filtrate and the washings were combined and evaporated. The residue was taken up in dil. HCl and the aqueous layer was washed with ether, neutralized (Na_2CO_3), and extracted with ether. Recrystallization of the product gave XIV as colorless prisms, m.p. 80~82°. Yield, 50 mg.

vii) Oxidative Desulfurisation of XVI by Hydrogen Peroxide in Acetic Acid——To a solution of 100 mg. of XVI in acetic acid (1 ml.) was added dropwise 35% hydrogen peroxide until no more turbidity occurred. The mixture was set aside at room temperature for 2 hr., filtered and the filtrate was concentrated under reduced pressure. The product, upon recrystallization from ether, formed colorless sticks, m.p. 119°, unchanged when mixed with an authentic sample of V. They also gave identical IR spectra.

3*α*-Methylaminoisoborneol (XV)——A mixture of 200 mg. of 3*α*-aminoisoborneol[8] and 1 ml. of 98% formic acid was refluxed for 5 hr., concentrated and extracted with $CHCl_3$. The extract was washed successively with 5% HCl, 5% aq. NaOH and H_2O, dried over anhydrous $MgSO_4$, and evaporated. Recrystallization of the residue from acetone-ether gave colorless needles of 3*α*-formamidoisoborneol, m.p. 162°. Yield, 150 mg. *Anal.* Calcd. for $C_{11}H_{19}O_2N$: C, 67.19; H, 9.71; N, 7.10. Found : C, 66.94; H, 9.94; N, 7.02. *α*-Formamidoisoborneol (480 mg.) was reduced in tetrahydrofuran with $LiAlH_4$ by the ordinary method to give XV (300 mg.) as colorless oil, which gradually crystallized from ether-hexane to form colorless plates, m.p. 66~67°. *Anal.* Calcd. for $C_{11}H_{21}ON$: C, 72.08; H, 11.55; N, 7.64. Found : C, 72.00; H, 11.59; N, 7.46. Hydrochloride, colorless needles, m.p. >310°. *Anal.* Calcd. for $C_{11}H_{21}ON \cdot HCl$: C, 60.12; H, 10.09. Found : C, 60.34; H, 10.14.

Acetylation of IV——IV (70 mg.) was treated with 2 ml. of pyridine and 1 ml. of Ac_2O under ice-water cooling. After standing for a week or so at room temperature, the brown reaction mixture was evaporated *in vacuo*, and the residue was recrystallized from ether to give 3-methyl-3*a*-acetoxy-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (XVII) as colorless scales, m.p. 120.5°. Yield, 60 mg. $[\alpha]_D^{30}$ +150.3°. ORD in MeOH (c=0.960) : $[\alpha]_{700}$ +120°, $[\alpha]_{600}$ +138°, $[\alpha]_{500}$ +212°, $[\alpha]_{400}$ +370°, $[\alpha]_{300}$ +860°. IR ν_{max}^{Nujol} cm^{-1} : 1753 (C=O), 1226, 1214, 1058, and 1027 (C-O). *Anal.* Calcd. for $C_{19}H_{21}O_4N$: C, 62.90; H, 7.92; N, 5.24. Found : C, 62.80; H, 8.10; N, 5.20.

On treatment with either NaOH or HCl, XVII was easily hydrolyzed to IV which was fairly stable to acid or alkali,

Chlorination of IV——a) A mixture of 100 mg of IV and 2 ml. of $SOCl_2$ was refluxed for 20 hr. until the gas evolution was ceased. After evaporation of the solution, the residue was taken up in benzene, washed with dil. HCl, H_2O, then dil. NaOH, and dried ($MgSO_4$). Removal of the solvent and recrystallization of the product from ether-hexane gave 3-methyl-3*a*,7*a*-dichloro-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (XVIII) as colorless rhombs, m.p. 132°. Yield, 100 mg. Insoluble in acid, alkali or water at room temperature. $[\alpha]_D^{28}$ −21.5° ($CHCl_3$). ORD in MeOH (c=0.960) : $[\alpha]_{700}$ −10°, $[\alpha]_{600}$ −15°, $[\alpha]_{500}$ −30°, $[\alpha]_{400}$ −40°, $[\alpha]_{300}$ −200°. IR ν_{max}^{Nujol} cm^{-1} : 1780 (C=O), 1030 (C−O), 845, and 812. *Anal.* Calcd. for $C_{12}H_{17}O_2NCl_2$: C, 51.81; H, 6.12; N, 5.04; O, 11.50; Cl, 25.49. Found: C, 51.68; H, 6.23; N, 5.05; O, 11.50; Cl, 25.77.

b) A mixture of IV (100 mg.) and PCl_5 (500 mg.) in $POCl_3$ (2 ml.) was refluxed for 20 hr., concentrated, decomposed with ice-water, and extracted with benzene. The residue after removal of the solvent was treated as described above to give colorless rhombs (80 mg.), m.p. 130~131°. This product was shown to be identical with the compound obtained in a) by comparison of the IR spectra and mixture melting point determination.

Acid Hydrolysis of XVIII——XVIII (400 mg.) was suspended into 10 ml. of 10% HCl and the mixture was heated at 100° for 15 hr. After cooling, the crystalline mass was collected and washed with cold dil. NaOH and then with H_2O, and dried. Recrystallization from MeOH-ether gave 3-methyl-3*a*-hyd-

roxy-7*a*-chloro-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (XIX) as colorless thin plates, m.p. 254° (decomp.). Yield, quantitative. $[\alpha]_D^{24}$ +13.3° ($CHCl_3$). ORD in MeOH (c=0.511): $[\alpha]_{700}$ +20°, $[\alpha]_{600}$ +20°, $[\alpha]_{500}$ +28°, $[\alpha]_{400}$ +40°, $[\alpha]_{300}$ +50°. IR ν_{max}^{Nujol} cm^{-1}: 3435 (OH), 1765 (C=O), 1113, 1032, and 1012. *Anal.* Calcd. for $C_{12}H_{17}O_2NClOH$: C, 55.49; H, 6.98; N, 5.39. Found: C, 55.45; H, 6.96; N, 5.16.

Alkaline Hydrolysis of XVIII and XIX——a) XVIII (260 mg.) was dissolved in 10 ml. of MeOH containing 620 mg. of KOH, and the solution was warmed at 75° for 4 hr., kept overnight at room temperature, and evaporated. The ether-soluble fraction was submitted to silica-gel chromatography, whereby yellow needles (100 mg.), m.p. 190~195°, were obtained. The identity with camphorquinone was established by mixture melting point determination and comparison of the IR spectra. From the $CHCl_3$ eluate fraction 100 mg. of XIX was obtained.

b) XIX (130 mg.) was dissolved in 3 ml. of abs. MeOH containing 200 mg. of Na, and the solution was left at room temperature for a week. A light yellow reaction mixture was obtained, which was concentrated *in vacuo*. The product was washed with $CHCl_3$, dissolved in H_2O (3 ml.), made acidic with HCl, and extracted with a large amount of ether. The extract, after drying over anhydrous $MgSO_4$ and evaporation, left a residue which was crystallized from ether-hexane to form colorless rhombs, m.p. 187°. Yield, 40 mg. $[\alpha]_D^{25}$ +46.1° (EtOH). This product was proved to be identical with an authentic sample of *d*-camphoric acid [m.p. 189°, $[\alpha]_D^{20}$ +47.7° (EtOH)] by mixture melting point determination and comparison of the IR spectra. A small amount of camphorquinone was obtained from the $CHCl_3$ extract. *Anal.* Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.22; H, 8.02.

The above product (10 mg.) was heated with 10 mg. of zinc chloride and 500 mg. of Ac_2O at 140° for 4 hr. After chromatography on silica-gel, colorless sticks (m.p. 220°, 3 mg.) were obtained by elution with ether. Admixture with an authentic sample of camphoric anhydride (m.p. 222°) showed no melting point depression.

Hydrogenation of XIX——a) To a solution of XIX (50 mg.) and KOH (50 mg.) in MeOH (10 ml.) was added 100 mg. of Raney-Ni, and the mixture was stirred under H_2 at room temperature and atmospheric pressure (uptake of H_2: 6 ml. within 1 hr.). After filtration from the catalyst the filtrate and the washings were combined and evaporated. The residue, after washing with H_2O, was crystallized from MeOH-ether to yield 37 mg. of colorless sticks, m.p. 188~190°. This product was proved to be identical with IV by mixture melting point determination and comparison of the IR spectra.

b) To a solution of XIX (130 mg.) in HOAc (6 ml.) was added under stirring at 100° 600 mg. of zinc. After 2 hr., additional 600 mg. of zinc was added and heating was continued for further 2 hr. After cooling, the reaction mixture was filtered and the residue was washed with MeOH. The filtrate and the washings were combined, concentrated, and extracted with $CHCl_3$. The $CHCl_3$ extract was washed successively with dil. aqueous ammonia, H_2O, dil. HCl, H_2O, dried ($MgSO_4$), and evaporated. The residue was chromatographed on alumina (neutral), and from the ether eluate fraction, the starting material (20 mg.) was recovered. Elution with acetone afforded a product as colorless sticks (45 mg.), m.p. 190~192°, which was proved to be identical with IV by mixture melting point and IR spectra determinations.

3-Methyl-3*a*-acetoxy-7*a*-chloro-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (XX)——a) A mixture of 40 mg. of XVIII, 60 mg. of silver acetate and 1 ml. of pyridine in acetic acid (1 ml.) was heated at 100° for 3 hr. The precipitated crystals were removed by filtration and the filtrate and the washings were concentrated and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with dil. aqueous ammonia, dried ($MgSO_4$) and evaporated. The residue was recrystallized from ether-hexane to give XX (25 mg.) as colorless plates, m.p. 84~85°. $[\alpha]_D^{22}$ +67.2° ($CHCl_3$). ORD in MeOH (c=0.567): $[\alpha]_{700}$ +57°, $[\alpha]_{600}$ +69° $[\alpha]_{500}$ +123°, $[\alpha]_{400}$ +192°, $[\alpha]_{300}$ +450°. IR ν_{max}^{Nujol} cm^{-1}: 1780 (C=O), 1750 (C=O), 1205, 1055, and 1030 (C-O). *Anal.* Calcd. for $C_{12}H_{17}O_2NClOCOCH_3$: C, 55.72; H, 6.68; N, 4.64. Found: C, 55.54; H, 6.76; N, 4.43.

b) To a solution of 50 mg. of XIX in 5 ml. of pyridine was added under cooling 1 ml. of Ac_2O, and the solution was kept at room temperature for a week. After recrystallization from ether-hexane the product was obtained as colorless plates (50 mg.), m.p. 84°, which was proved to be identical with the compound obtained in a) by mixture melting point determination and comparison of the IR spectra. Treatment of either XVIII or XX with excess of silver acetate in pyridine resulted in obtaining XX.

XX (20 mg.) was heated with 2 ml. of 10% HCl on a steam bath for 4 hr. The product was recrystallized from ether to give colorless thin plates, m.p. 254° (decomp.), and was identified as XIX.

Chlorination of XIX with Thionyl Chloride——A mixture of 50 mg. of XIX and $SOCl_2$ (2 ml.) was refluxed for 20 hr., concentrated, and the product was recrystallized from ether-hexane to form colorless plates, m.p. 132°, identical with XVIII.

3-Methyl-3*a*-methoxyl-7*a*-chloro-3*aβ*, 7*aβ*-bornano[3, 2-*d*]oxazolidin-2-one (XXI)——a) A mixture of XVIII (40 mg.), silver nitrate (60 mg.), pyridine (2 ml.) and MeOH (2 ml.) was heated on a steam bath for 1.5 hr. until no further precipitation of solid occurred. After filtration the filtrate was concentrated and extracted with benzene, and the organic layer was washed with water, then dil. aqueous ammonia and dried over anhydrous $MgSO_4$. The oily residue after removal of the solvent was distilled *in vacuo*, $b.p._{0.05}$ 110~120°, and the distillate crystallized on standing in colorless rhombs, m.p. 76~78° (hexane). ORD in MeOH (c=0.371): $[\alpha]_{700}$ +0.4°, $[\alpha]_{600}$ +0.67°, $[\alpha]_{500}$ +0.67°, $[\alpha]_{400}$ +1.07°, $[\alpha]_{300}$ +2.6°. IR ν_{max}^{Nujol} cm^{-1}: 1768 (C=O), 1103 (CH_3O), and 1030 (C-O). *Anal.* Calcd. for $C_{12}H_{17}O_2NClOCH_3$: C, 57.03; H,

7.36. Found : C, 56.87; H, 7.53.

b) XVIII (20 mg.) was heated with 2 ml. of 25% methanolic hydrogen chloride for 5 hr. The solution was concentrated and distilled *in vacuo*, b.$p_{0.05}$ 115° (12 mg.). The product obtained was proved to be identical with XXI by direct comparison of their IR spectra.

Catalytic Hydrogenation of XXI——XXI (50 mg.) was reduced catalytically in MeOH in the presence of Raney-Ni (100 mg.) at room temperature and atmospheric pressure (uptake of H_2, 1 mol.) The reaction product was worked up by the ordinary method to give 3-methyl-3*a*-methoxy-3*aβ*,7*aβ*-bornano[3,2*d*]-oxazolidin-2-one (XXII), b.$p_{0.5}$ 120~130°, m.p. 48~50° (soluble in organic solvents). IR ν_{max}^{Nujol} cm^{-1} : 1760, 1132, 1085, and 1050. *Anal.* Calcd. for $C_{13}H_{21}O_3N$: C, 65.24; H, 9.02. Found : C, 65.19; H, 9.03.

Hydrogenation of XIX with Zinc in CH_3COOD——To a solution of 260 mg. of XIX in CH_3COOD (prepared from 10 ml. of Ac_2O and 3 ml. of deuterium oxide) was added under stirring at 110° 1 g. of zinc. After 1.5 hr., 1.5 g. of zinc was added and heating was continued for further 4.5 hr. The reaction mixture was filtered and the zinc was washed with EtOH. The filtrate and the washings were combined, concentrated, extracted with $CHCl_3$, and the organic layer was washed successively with dil. HCl, dil. NaOH, and H_2O, and dried over anhydrous K_2CO_3. After removal of the solvent and recrystallization XXIII was obtained as colorless sticks, m.p. 192~193°, undepressed by admixture with a sample of IV, and their IR spectra were virtually identical

Catalytic Hydrogenation of XVIII with Palladium-charcoal——A mixture of 100 mg. of XVIII and 200 mg. of KOH in 10 ml. of MeOH was reduced catalytically over 10% palladium-charcoal (100 mg.) at room temperature and atmospheric pressure (uptake of H_2 : 2 mol. = 16 ml. within 15 min.). After filtration from the catalyst the filtrate was concentrated and extracted with ether. The ether solution was washed with dil. HCl and then with H_2O. (From the aqueous layer XIV (13 mg.), m.p. 84~85°, was obtained after being made alkaline and extraction with ether.) After removal of the solvent the product was recrystallized from ether-hexane to give colorless sticks, m.p. 119° (60 mg.), identical with V by mixture melting point determination and comparison of the IR spectra.

Catalytic Hydrogenation of XVIII with Raney Nickel——A mixture of 55 mg. of XVIII and 100 mg. of KOH in 10 ml. of MeOH was stirred under hydrogen in the presence of Raney-Ni (200 mg.) at room temperature and atmospheric pressure (uptake of H_2 : 2 mol. = 9 ml. within 15 min.). The catalyst was filtered off and the filtrate was concentrated *in vacuo*. The residue was taken up in ether, washed with dil. HCl (From this aqueous layer, no basic substances were detected.) and then with H_2O. The ether solution, after drying over anhydrous $MgSO_4$ and evaporation, left a crystalline residue, which was recrystallized from ether to give 3-methyl-3*aα*,7*aα*-bornano[3,2-*d*]oxazolidin-2-one (VI) of colorless sticks, m.p. 123°. Yield, 28 mg. $[\alpha]_D^{27}$ −33.3° ($CHCl_3$). ORD in MeOH (c = 0.502) : $[\alpha]_{700}$ −10°, $[\alpha]_{600}$ −18°, $[\alpha]_{500}$ −40°, $[\alpha]_{400}$ −56°, $[\alpha]_{300}$ −90°. IR ν_{max}^{Nujol} cm^{-1} : 1740 (C=O), 1238, and 1036 (C-O). *Anal.* Calcd. for $C_{12}H_{19}O_2N$: C, 68.86; H, 9.15; N, 6.69. Found : C, 68.94; H, 9.36; N, 6.53.

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Summary

In connection with the structure elucidation of two products, 3-methyl-7*a*-chloro-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (III) and 3-methyl-3*a*-hydroxy-3*aβ*,7*aβ*-bornano-[3,2-*d*]oxazolidin-2-one (IV), obtained by the reaction of 3*α*-methylaminocamphor (I) with phosgene, 3-methyl-3*aβ*,7*aβ*-bornano[3,2-*d*]oxazolidin-2-one (V), 3-methyl-3*aα*,7*aα*-bornano[3,2-*d*]oxazolidin-2-one (VI) and their derivatives were synthesized and studied stereochemically. Their proton magnetic resonance spectra were also investigated.

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