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253. Takuo Okuda and Takashi Yoshida*1 : The Correlation of Coriamyrtin and Tutin, and Their Absolute Configurations.*2

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The structural correlation of coriamyrtin (I) and tutin (II) was established by deriving both compounds to coriamyrtin-isonorketone-methoxide (XXVIII), as well as to its dihydro derivative (XXX). The absolute configurations of these compounds were determined by the ORD spectra and the benzoate rule. The mutual influences of the 2-hydroxyl group and the terminal epoxide in the NMR spectra were analyzed for tutin and derivatives.

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The relative configurations of coriamyrtin were shown to be as in formula (I) in the preceding paper.*3 The correlation of this structure with the structure (II) of tutin, which was recently proposed on the basis of the X-ray crystallography of α-bromoisotutin (III)[1] and α-bromoisotutinone (IV),[2] is in agreement with our previous assumption that tutin is a hydroxycoriamyrtin,[3] although there has been no direct evidence for this correlation. The authors wish to present here the establishment of this correlation, and the complete absolute configurations of coriamyrtin and tutin, which are represented by I and II, respectively.

Table I. Chemical Shifts of the Angular Methyl and the Terminal Epoxide Protons

Compound	1-CH_3 (τ)		14-H (τ, AB quartet)	
	pyridine	$CHCl_3$	pyridine[d]	J_{AB} (c/s)
Coriamyrtin (I)	8.52	8.85	6.69, 6.92	4
Dihydrocoriamyrtin (VI)	8.50	8.80	6.70, 6.92	4
α-Bromocoriamyrtin (VII)	8.46[a] (8.42)	8.67[a,b] (8.40)	6.72, 6.95	4
Apocoriamyrtin (VIII)	8.50[a] (8.61, 8.66)	8.68[a,b] (8.49, 8.60)	6.71, 6.97	4
Acetoxyapocoriamyrtin (IX)	8.59[a] (8.46)	8.69[a] (8.55)	6.72, 6.95	4
Tutin (II)	8.06	8.58[b]	5.29, 6.90	6
Dihydrotutin (X)	8.02	8.54	5.24, 6.92	6
α-Bromotutin (V)	8.08[c]	8.43	5.35, 7.01	6
Acetyltutin (XI)	8.32	8.72	5.92, 6.90	6
Tutinone (XII)	8.29	8.70	6.93, 7.20	4

a) Exclusive evidence has not been obtained as to which one of the two or three peaks, in and out of the parentheses, is due to 1-CH_3.
b) Obtained in $CDCl_3$.
c) Between two methyl peaks at 8.45 τ and 8.42 τ, the lower one which showed the large downfield shift upon stepwise dilution with pyridine was assigned to 1-CH_3. The other methyl peak (8.46 τ in 100% $CHCl_3$) showed only a small shift.
d) Owing to the low solubility of tutin in $CHCl_3$, the shift of 14-H of tutin and derivatives in this solvent has not been recorded.

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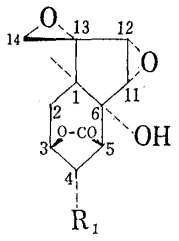
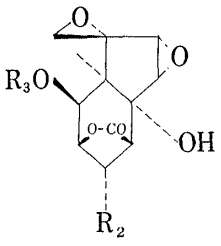
*2 This paper constitutes Part XII of "Coriamyrtin,"*3 which is Part XVIII of a series entitled "Studies on the Components of *Coriaria japonica* A. Gray." Preliminary reports of this work have been published: Tetrahedron Letters, **1965**, 2137, 4191.

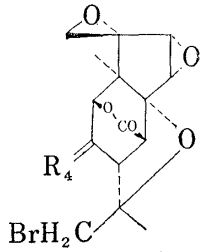
*3 Part XI : This Bulletin, **15**, 1697 (1967).

1) B.M. Craven : Nature, **1963**, 1193.
2) M.F. Mackay, A.M. Mathieson : Tetrahedron Letters, **1963**, 1399.

The assumption made on the structure elucidation of tutin that α-bromoisotutin arises from α-bromotutin (V) by the transformation of the γ-lactone to the δ-lactone without being accompanied by any other major structural change is substantiated as follows : The nuclear magnetic resonance (NMR) spectrum of tutin is analogous to that of coriamyrtin except that C-2 proton in tutin is shown at 5.26τ (in pyridine), and that marked downfield shift of the angular methyl signal and also of one of the two protons in the terminal epoxide is exhibited by tutin and derivatives (Table I). The spin-spin coupling of the doublet at 6.90τ with the doublet at 5.29τ in tutin has been confirmed by the double-resonance method. As shown in Table I, the large downfield shift in pyridine is exhibited by the compounds which have a free hydroxyl group at C-2. The solvent shifts of the angular methyl signal in these compounds are larger than most of those reported for



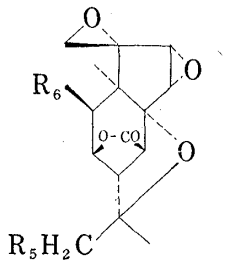


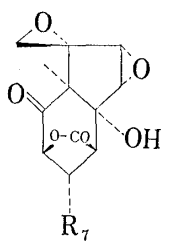


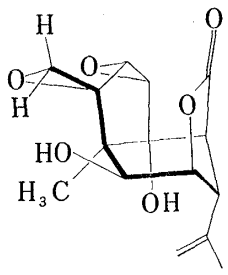
I : R_1=CMe=CH_2 [*3]
VI : R_1=$CHMe_2$ [4]

II : R_2=CMe=CH_2, R_3=H
X : R_2=$CHMe_2$, R_3=H [3]
XI : R_2=CMe=CH_2, R_3=Ac [3]
XXXIII : R_2=CMe=CH_2, R_3=Bz

III : R_4=—H, —OH [1]
IV : R_4=O [2]







V : R_5=Br, R_6=OH [3]
VII : R_5=Br, R_6=H [*3]
VIII : R_5=R_6=H [4]
IX : R_5=AcO, R_6=H [*3]

XII : R_7=CMe=CH_2 [*4]
XIV : R_7=$CHMe_2$ [*4]

IIa

Chart 1.

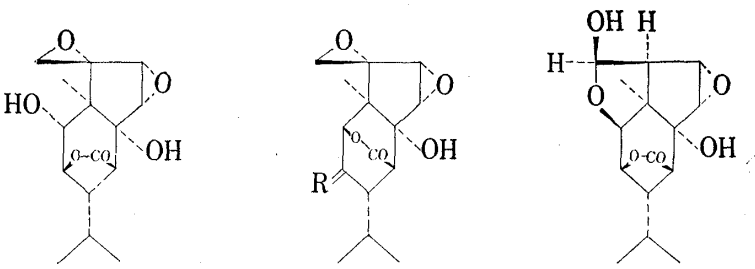
the compounds in which the angular methyl group is closely situated to a hydroxyl group.[5] Although such a large solvent shift of the methyl signal may be rather unusual for the structures such as II and derivatives, in which the hydroxyl group is oriented *trans* to the methyl group, the β-configuration of 2-OH is consistent with the low shift of the epoxide proton since one of the two hydrogens of the terminal epoxide is located

[*4] Prepared by the method of J.R. Fletcher, *et al.* : J. Chem. Soc., **1954**, 1953. The IR and NMR spectra, which show the retention of the two epoxides and the γ-lactone, were in accord with the structure depicted above.

3) T. Okuda : This Bulletin, **2**, 185 (1954).
4) T. Okuda, T. Yoshida : *Ibid.*, **15**, 1687, 1697 (1967).
5) K. Tori, Y. Hamashima, A. Takamizawa : This Bulletin, **12**, 924 (1964); G. Slomp, F. MacKellar : J. Am. Chem. Soc., **82**, 999 (1960); T.J. Flautt, W.F. Erman : *Ibid.*, **85**, 3212 (1963).

near 2-βOH when the cyclohexane ring in tutin takes the *quasi*-chair conformation (IIa) like that in coriamyrtin.[*3] The stereomodel[*5] indicates that the distortion of the ring makes the angle between the β-hydroxyl group and the methyl group markedly smaller. Although 6-OH, 2-OH, 2-carbonyl, 2-OAc, 8-CH_2Br and the terminal epoxide, which are situated near the angular methyl group might be participating in producing the low shifts of the methyl signal of tutin and derivatives, the solvent shift by the presence of 2-OH should be the major factor in causing the difference of the methyl shift between coriamyrtin and tutin. Thus the pyridine molecule, which is hydrogen-bonded to 2-OH, might be spatially confined by the steric requirement of the epoxide, the lactone and the other groups in such a way to give the strong paramagnetic anisotropy effect to the angular methyl group.

Preparation of (XIII), which is C-2 epimer of dihydrotutin, by sodium borohydride reduction of dihydrotutinone (XIV), was then attempted, and a compound which is regarded as being the epimer was obtained as a minor product: The major product, $C_{15}H_{20}O_6$, is presumed to be the δ-lactone (XV), on the basis of the IR absorption at 1736 cm^{-1}, the NMR spectrum (in pyridine), which shows 2-H at 5.38τ as a diffused singlet, and 3-H at 5.60τ as a diffused doublet (J=6 c/s), and also of the chromic acid oxidation which gave a product, $C_{15}H_{18}O_6$, IR ν_{max}^{KBr} cm^{-1}: 1763, 1736,[*6] which was not identical with dihydrotutinone. The reduction product XV was therefore named isodihydrotutin, and the ketone which is presumably shown by the structure (XVI), was named isodihydrotutinone. The upfield shift of the angular methyl peak to 8.73τ, and of the terminal epoxide signals to 6.81τ (J=4 c/s) and 6.66τ (J=4 c/s) in the NMR spectrum of XV, are considered to be due to the conformational changes induced by the transformation of the lactone. The minor product, which was also found to be different from dihydrotutin, is presumed to be XIII based on the infrared (IR) band of γ-lactone at 1762 cm^{-1} and the NMR spectrum (in pyridine) which shows the terminal epoxide protons at 6.93τ (J=4 c/s) and 6.54τ (J=4 c/s), indicating absence of the strong influence by 2-βOH, and also on the result of chromic acid oxidation which produced dihydrotutinone. The angular methyl peak at 8.09τ in XIII, which is now called epidihydrotutin, shows that the downfield shift induced by the presence of 2-αOH, which is *cis* to the methyl group, is somewhat smaller than that caused by 2-βOH, although the extent of the former is also larger than most of the reported compounds.



XIII XV : R=—H, —OH XVII

XVI : R=O

Chart 2.

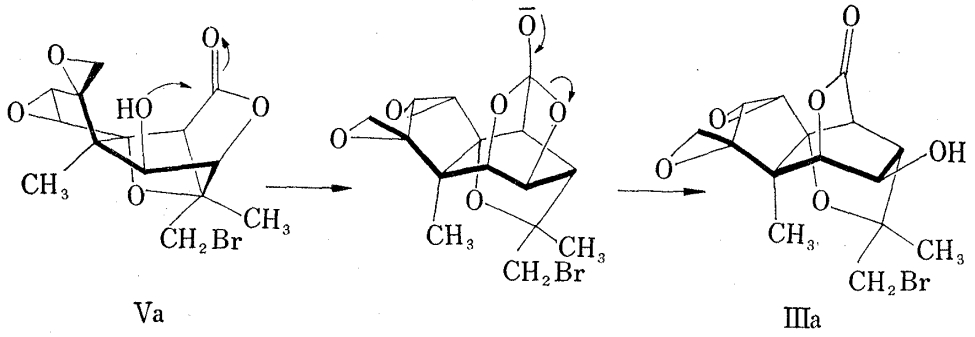
An additional evidence for the steric correlation of 2-OH and the terminal epoxide has been provided by the following transformation: Dihydrotuin X was heated in dilute sulfuric acid to produce an isomer (XVII), $C_{15}H_{20}O_6$, whose IR spectrum shows presence of the hydroxyl and the γ-lactone group, and absence of the double bond. The NMR spectrum is indicative of retention of the epoxide at C-11~C-12. By the double-resonance method (in $CDCl_3$), a doublet at 4.47τ (1H, J=7 c/s) which could be an acetal proton was shown to be spin-coupled with the proton at 7.44τ (d, J=7 c/s, 13-H). The

[*5] The Dreiding stereomodel was used.

[*6] Carbonyl absorptions of α-bromoisotutinone IV, ν_{max}^{Nujol} cm^{-1}: 1778, 1760, 1740.

spin-spin coupling of the diffused triplet at 5.27τ (1H, J=4 c/s, 3-H) with the doublet at 5.99τ (1H, J=4 c/s, 2-H), and the coupling of the doublet at 6.44τ (1H, J=2.5 c/s, 11-H) with the diffused doublet at 6.08τ (J=2.5 c/s, 12-H) were also proved by the NMDR technic. The 14-hydrogen may rather be α-oriented when the observation of the stereomodel which indicates that the angle $\angle$14-αH$\sim$13-αH is *ca.* 10°, while the angle $\angle$14-βH$\sim$13-αH is *ca.* 105°, is taken into consideration. The appearance of 13-H as a doublet with small splitting of the peaks may be due to the angle $\angle$13-H$\sim$12-H, which is approximately 90°. The structure of the isomerized product thus shown by XVII is in accord with the β-configuration of 2-OH in tutin.

The transesterification V→III, which was carried out in alkali without neutralization, or by treating V with diazomethane,[6] then may be shown as Va→IIIa.



Va IIIa

Chart 3.

The correlation, that tutin is 2-hydroxycoriamyrtin has been established by the elimination of the hydroxyl group. The initial attempts to eliminate 2-OH from tutin II, dihydrotutin X, and α-bromotutin V *via* mesyl or halogen derivatives, or to reduce the thioketals of the 2-ketones were unsuccessful probably because of the steric hindrance at C-2, and also of the lability of the epoxides on drastic reactions. The steric hindrance at C-2 has been shown by the recovery of tutinone and other 2-ketones from the reaction with the carbonyl reagents.

The elimination of 2-OH after producing a double bond at C-3$\sim$C-4 was then attempted. By the ozonolysis of tutin, tutin-norketone (XVIII), $C_{14}H_{16}O_7$, which shows the presence of a methyl ketone by the UV, IR, and NMR spectra, was obtained. The NMR spectrum also exhibits the retention of the steric correlation between the terminal epoxide and 2-OH of tutin by the low shift of the angular methyl signal and of one of the terminal epoxide protons. A doublet is shown at 6.19τ (J=2.5 c/s), which is assignable to 5-H. This downfield shift may be due to the anisotropy effect by 8-ketone. The β-elimination of the norketone XVIII was performed in the presence of a trace of sodium methoxide in methanol to produce tutin-isonorketone (XIX), $C_{14}H_{16}O_7$. In addition to the UV and IR spectra which show the presence of the α,β-unsaturated ketone, the NMR spectrum (in pyridine-d_5) which shows a doublet at 2.48τ (1H, J=6 c/s) spin-coupled with a proton at 5.33τ (1H, d, J=6 c/s), is also in agreement with the formation of a double bond at C-3$\sim$C-4. The epoxide protons at C-11 and C-12 of XVIII has been replaced by a lower AB quartet at 4.53τ and 4.39τ (J=4 c/s), while the signals of the terminal epoxide are retained with modified pattern (6.89τ, s). The upfield shift of the angular methyl signal is also observed. These shifts of the terminal epoxide and the angular methyl protons are attributable to the conformational change. The IR absorption at 1775 cm^{-1} (in $CHCl_3$) indicates that the new lactone is bridged between

6) J.C. Benstead, H.V. Brewerton, J.R. Fletcher, M. Martin-Smith, S.N. Slater, A.T. Wilson: J. Chem. Soc., **1952**, 1042.

C-5 and C-11. A further downfield shift of 5-H (5.04τ, s) is also shown in the NMR spectrum. The NMR spectrum measured in dimethylsulfoxide exhibits a singlet and two doublets, which disappear on addition of D_2O, to be indicative of the presence of a tertiary and two secondary hydroxyl groups. These spectral evidences are in accord with the structure XIX, and this transformation is, therefore, similar in the main part to the transformation of α-picrotoxinone to β-picrotoxinone.[7]

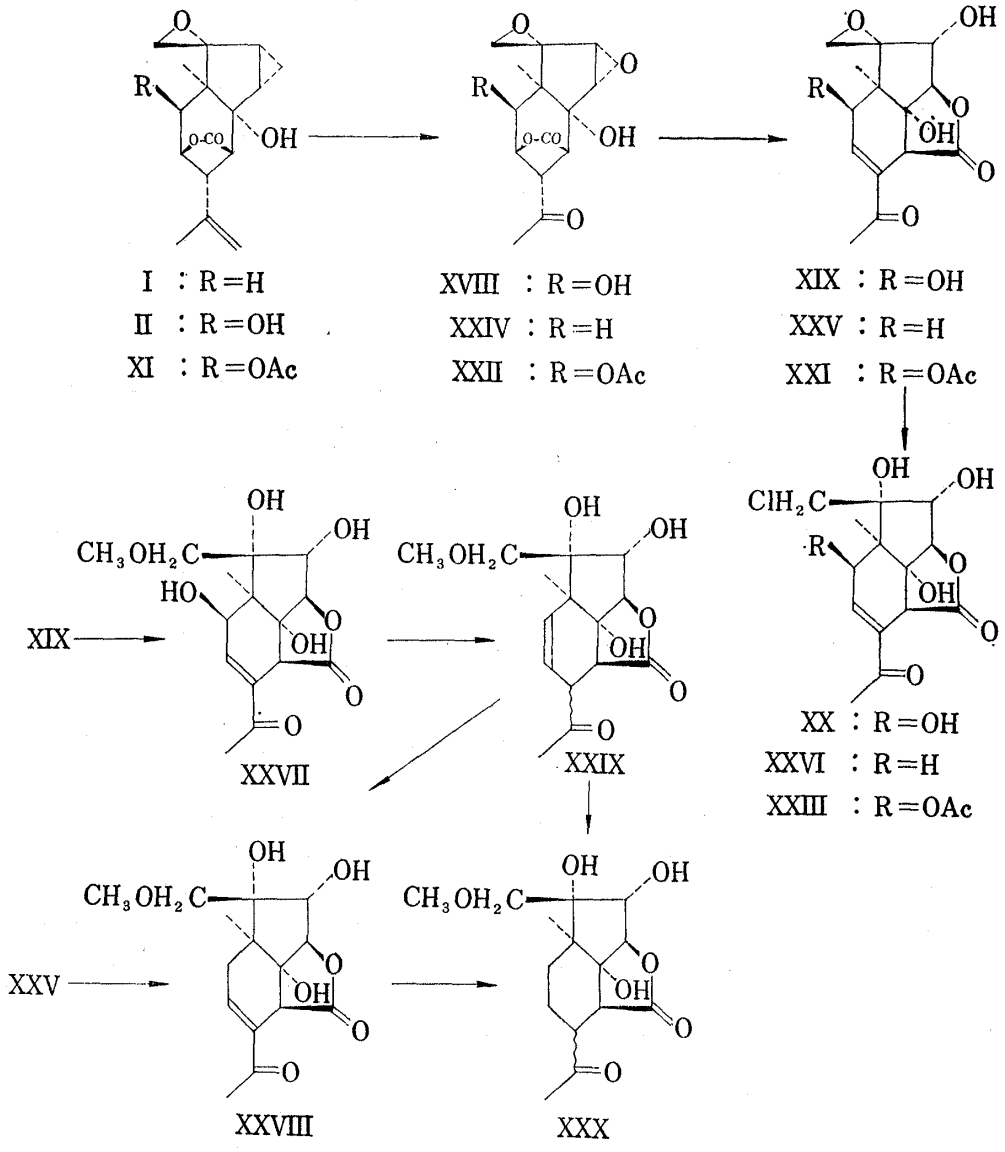


Chart 4.

It is now presumable that the stability of the terminal epoxide has been lowered by this transformation owing to the removal of the lactone carbonyl from the back side of the epoxide. Indeed, the initial attempts to eliminate 2-OH of XIX by the hydrogenolysis over palladium-charcoal catalyst in acetic acid resulted in the opening of the terminal epoxide to provide the chlorohydrin (XX), $C_{14}H_{17}O_7Cl$. The NMR spectrum (in DMSO-d_6) of this product shows absence of the terminal epoxide, and appearance of an AB quartet at 6.24τ and 6.02τ (J=12 c/s), which is assignable either to $-\overset{|}{\underset{|}{C}}-CH_2Cl$ or $\overset{|}{\underset{OH}{C}}$

7) P.I. Burkhill, J.S.E. Holker : J. Chem. Soc., **1960**, 4011.

$-\overset{|}{C}-CH_2OH$, of which the former is preferred by analogy with XXVI, XXVII, and XXVIII.
Cl

The NMR spectrum also indicates that the other part in the molecule is identical with the corresponding part of XIX. The same chlorohydrin was obtained by treating XIX with hydrochloric acid in acetic acid. This chlorohydrin was fairly resistant to further hydrogenation over platinum catalyst.

The hydrogenolysis was also attempted with acetyltutin-isonorketone (XXI), which was produced by the analogous transformation from acetyltutin-norketone, $C_{16}H_{18}O_8$ (XXII), prepared by the ozonolysis of acetyltutin XI. However, the only product isolated from this attempt was the corresponding chlorohydrin, $C_{16}H_{19}O_8Cl$ (XXIII).

The ozonolysis of coriamyrtin afforded coriamyrtin-norketone (XXIV), $C_{14}H_{16}O_6$, whose spectra show the presence of a methyl ketone. The norketone XXIV was then converted into coriamyrtin-isonorketone (XXV), $C_{14}H_{16}O_6$, by the reaction analogous to the transformation of XVIII to XIX. This isonorketone provided the chlorohydrin (XXVI), $C_{14}H_{17}O_6Cl$, whose NMR spectrum measured in DMSO-d_6 exhibits two singlets and one doublet, which disappear by the addition of D_2O, to show that a secondary and two tertiary hydroxyl groups are present.

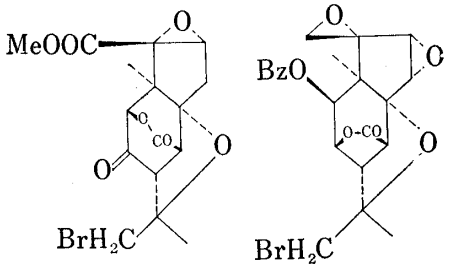
The terminal epoxide in these isonorketones was then converted into the stable methoxymethylene group in advance to further attempts to eliminate 2-OH. Tutin-isonorketone XIX was treated with methanol containing perchloric acid to produce the methoxyl derivative (XXVII), $C_{15}H_{20}O_8$, whose NMR spectrum shows a methoxyl signal at 6.70τ, and a newly formed AB quartet at 6.59 and 6.32τ (J=11 c/s, 14-H×2), and the absence of the terminal epoxide. Coriamyrtin-isonorketone XXV was also converted to the methoxyl derivative (XXVIII), $C_{15}H_{20}O_7$, whose NMR spectrum (in DMSO-d_6) shows the methoxymethylene protons at 6.72τ (3H), and 6.63τ (s, 2H). The NMR spectra of these methoxyl derivatives measured in dimethylsulfoxide indicate the presence of two secondary and two tertiary hydroxyl groups in XXVII, and a secondary and two tertiary hydroxyl groups in XXVIII showing that the methoxyl group has been introduced at C-14 of these compounds.

The attempted hydrogenolysis of XXVII again provided no recognizable amount of the expected elimination product. However, the treatment of XXVII with zinc dust in refluxing acetic acid produced an elimination product (XXIX), $C_{15}H_{20}O_7$, m.p. 183~185°, of which the presence of the isolated ketone and the double bond is shown by the ultraviolet (UV) absorption, λ_{max}^{MeOH} 283 mμ (log ε 1.96), and IR absorptions at 1707 and 1640 (shoulder) cm^{-1}. The NMR spectrum exhibits two olefinic protons which form an ABX system with 4-H (3.90τ,q, J_1=10 c/s, J_2=6 c/s, 3-H; 3.52τ, d, J=10 c/s, 2-H; 5.98τ, diffused doublet, J=6 c/s, 4-H). Therefore, the double bond should have been transferred to C-2~C-3. This elimination product was then hydrogenated over palladium-charcoal catalyst in methanol to absorb one mole of hydrogen to afford the product (XXX), $C_{15}H_{22}O_7$, $[\alpha]_D^{25}$ +65.7°, of which the saturation of the double bond is shown by the IR and NMR spectra. The ORD spectrum of this product shows a positive rotation maximum at 300 mμ ($[\phi]_D^{25}$ +3,740°). A yellow 2,4-dinitrophenylhydrazone, $C_{21}H_{26}O_{10}N_4$, was produced. This saturated derivative XXX was also derived from coriamyrtin-isonorketone-methoxide XXVIII either by hydrogenation over palladium-charcoal catalyst absorbing one mole of hydrogen, or by zinc dust reduction in acetic acid. The product thus obtained from XXVIII was identical with XXX in all respects. An additional proof of the structural correlation of coriamyrtin and tutin was obtained by isomerization of XXIX to XXVIII, performed by refluxing XXIX with potassium acetate in ethanol. The identification of the product with XXVIII was again established in every respect.

Although the identity of the configurations at C-4 is not proved by the above-mentioned transformations, the identity of this part has already been substantiated by

the reactions such as the ether formation,[3,4] the isomerizaton in mineral acids,[4] and the lead tetraacetate oxidation,*3 The correlation, that tutin is 2-β-hydroxycoriamyrtin, has accordingly been established.

The determination of the absolute configurations of tutin has been made by the use of the optical rotatory dispersion and also by the application of the benzoate rule.[8] α-Bromoisotutinone Ⅳ has shown a negative rotation maximum at 346 mμ ($[\phi]^{20}$ −4,760°, c=0.374, dioxane), and the curve was almost superposable on that of methyl β-bromo-oxopicrotoxinate[9] ($[\phi]^{20}_{346}$ −5.480°, c=0.392, dioxane) whose absolute configurations are shown by (XXXI)*3 based on the X-ray crystallography of α_1-bromopicrotoxinin. The analogy between these two curves indicates the absolute configurations of tutin to be represented by Ⅱ. The benzoate rule has been applied to α-bromotutin and tutin. Benzoyl α-bromotutin (XXXII), $C_{22}H_{21}O_7Br$, of which the introduction of the benzoyl group to 2-oxygen without any other structural change is shown by the IR and the NMR spectra, was obtained by the reaction of α-bromotutin with benzoyl chloride in pyridine. In applying the benzoate rule, it could be regarded that the C-1 part is the lesser polarizable and the larger group, and the C-3 part is the more polarizable as well as the smaller group. Although the requirements of the terminal epoxide, the lactone and the other groups which are sterically near the benzoyl group will also have to be taken into consideration, the stereomodel shows that the benzoyl group should tend to be flanked by 2-H and C-3 by the requirement of the groups mentioned above. Accordingly, all of these effects could provide analogous effects to produce levorotatory shift. The observed molecular rotations of α-bromotutin ($[M]^{20}_D$ −502°, c=0.85, dioxane) indicates the rotation difference to be −338° showing that the absolute configuration at C-2 is in accord with the assignment of Ⅴ to α-bromotutin, and therfore, Ⅱ to tutin. The rotation difference between benzoyltutin (XXXIII), $C_{22}H_{22}O_7$,*7 ($[M]^{20}_D$ +14°, c=0.427, dioxane) and tutin ($[M]^{15}_D$ +73°, c=0.937, dioxane) was observed to be −59°, providing a further proof of the absolute configurations of tutin represented by Ⅱ. These results are in accord with the absolute configurations of α-bromoisotutin Ⅲ proposed by Craven in his later paper on the basis of the X-ray crystallography.[10]



XXXI XXXII

Chart 5.

The absolute configurations of coriamyrtin, which have been correlated with those of tutin as mentioned above, should consequently be represented by Ⅰ.

Experimental*8

Sodium Borohydride Reduction of Dihydrotutinone (XIV)——To a solution of dihydrotutinone (550 mg.) in MeOH (25 ml.) was added $NaBH_4$ (200 mg.). After standing for 24 hr. at room temperature, AcOH was

*7 First reported by K. Kinoshita : Nippon Kagaku Zasshi, **51**, 99 (1930), to have the molecular formula, $C_{19}H_{18}O_6$.

*8 Melting points are uncorrected. NMR spectra were determined on a Varian Associates recording spectrometer (A-60) at 60 Mc. Chemical shifts were recorded in τ values, using tetramethylsilane as the internal reference. IR spectra were measured in mineral oil suspension unless otherwise specified. $[\alpha]_D$ was recorded with a Rex Photoelectric Polarimeter. ORD curves were measured with a Japan Spectroscopic Company ORD/UV-5 spectropolarimeter. Neutral alumina (Woelm) and silicic acid (Mallincrodt) were used for elution chromatography. Darco G 60 (Merck) was used for the preparation of Pd-C catalyst.

8) J.H. Brewster : Tetrahedron, **13**, 106 (1961).
9) M. Sutter, E. Schlittler : Helv. Chim. Acta, **33**, 902 (1950); R.M. Carman, G. Hassan, R.B. Johns : J. Chem. Soc., **1959**, 130.
10) B.M. Craven : Acta Cryst., **17**, 396 (1964).

added, and the mixture was distilled *in vacuo*. Water was added to the residue, and the resultant solution was extracted with $CHCl_3$. The $CHCl_3$ solution was dried over $MgSO_4$, and distilled to give an oily residue, whose thin-layer chromatography (Silica gel G acc. to Stahl, E. Merck; $CHCl_3$–acetone, 27:5) showed two main spots. A minor spot corresponding to dihydrotutin was shown between the two main spots, and another minor spot which moved slower than the other three was also observed. This residue was chromatographed on a column of silicic acid (30 g., 14.5×3 cm.) using $CHCl_3$ and then $CHCl_3$–acetone as eluants. The crystalline residue from the fractions eluted with $CHCl_3$–acetone (95:5) was recrystallized from EtOH to provide colorless crystals of (XIII), m.p. 254° (decomp.) (9 mg.). IR ν cm^{-1}: 3430 (OH), 1762 (γ-lactone). $NMR^{pyridine}_{max}(\tau)$: 8.77 (d, J=7 c/s), 8.73 (d, J=7 c/s) (Me_2CH–); 8.09 (s, Me–$\overset{|}{\underset{|}{C}}$–); ABq, 6.92, 6.54 (J=4 c/s, 14-H×2); ABq, 6.39, 5.88 (J=3 c/s, 11~12-H×2). Mixed melting point and IR comparison also showed that this product is different from dihydrotutin. To a solution of this product (7 mg.) in acetone (2 ml.) was added a solution of CrO_3 in dilute H_2SO_4,[11] until persistent coloration. Water was added 30 min. later, and then the mixture was extracted with $CHCl_3$. The $CHCl_3$ solution was dried over $MgSO_4$, and distilled. Crystalline residue was recrystallized from EtOH–petr. ether to yield colorless needles, m.p. 257° (decomp.) (2 mg.) (IR ν cm^{-1}: 3370, 1800, 1700), which were identified with dihydrotutinone by mixed melting point and IR comparison.

Another product (XV), which moved slower than XIII, was eluted by the same solvent mixture, being partially overlapped by the latter. Recrystallization from EtOH–petr. ether afforded colorless crystals, m.p. 230~231° (58 mg.). *Anal.* Calcd. for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.58; H, 7.01. IR ν cm^{-1}: 3360 (OH), 1736 (δ-lactone). $NMR^{pyridine}_{max}(\tau)$: 8.86 (d, J=7 c/s), 8.68 (d, J=7 c/s) (Me_2CH–); 8.71 (s, Me–$\overset{|}{\underset{|}{C}}$–); ABq, 6.81, 6.66 (J=4 c/s); ABq, 6.37, 5.90 (J=3 c/s); 5.62 (diffused doublet, J=5 c/s, 3-H); 5.36 (diffused singlet). Oxidation of this product (XV) (15 mg.) with chromic acid as above yielded a crystalline product which was recrystallized from EtOH–petr. ether. m.p. 216° (9 mg.). *Anal.* Calcd. for $C_{15}H_{18}O_6$: C, 61.21; H, 6.17. Found: C, 61.11; H, 6.42. IR ν cm^{-1}: 3450, 1763, 1736.

Isomerization of Dihydrotutin in Sulfuric Acid——To finely ground dihydrotutin (500 mg.), 1.5% H_2SO_4 (30 ml.) was added, and the mixture was heated on a boiling water-bath for 5 hr. The resultant solution was neutralized with $NaHCO_3$, and extracted with ether. The dried ether solution was distilled to provide an oily residue which was dissolved in $CHCl_3$, and poured on a column of silicic acid (2×12 cm.). Crystalline residue obtained on evaporation of the eluate was recrystallized from $CHCl_3$–petr. ether to afford colorless crystals of (XVII), m.p. 187~188° (45 mg.). *Anal.* Calcd. for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 61.07; H, 6.91. IR ν^{KBr}_{max} cm^{-1}: 3370, 3510 (OH); 1781 (γ-lactone).

Tutin-norketone (XVIII)——Ozonized oxygen was conducted through the solution of tutin (1.0 g.) in EtOAc (100 ml.) at −70° for 8 hr. The resultant solution was left to stand to reach room temperature, and then was hydrogenated over Pd-C, prepared from 5% $PdCl_2$ solution (3 ml.) and charcoal (1.2 g.) in MeOH (*ca.* 10 ml.), to absorb 1 mole of hydrogen. Distillation of the solvent *in vacuo* yielded a crystalline residue which was recrystallized from MeOH to afford colorless crystals, m.p. 215° (decomp.) (0.92 g.). *Anal.* Calcd. for $C_{14}H_{16}O_7$: C, 56.75; H, 5.44. Found: C, 56.89; H, 5.61. $[\alpha]_D^{34}$ −27.3° (c=0.915, EtOH). UV λ^{MeOH}_{max} mμ (log ε): 270 (1.48). IR ν cm^{-1}: 3400, 3280 (OH); 1752 (γ-lactone); 1695 (ketone). $NMR^{pyridine}_{max}(\tau)$: 8.10 ($CH_3$–$\overset{|}{\underset{|}{C}}$–); 7.51 ($CH_3CO$–); ABq, 6.93, 5.24 (J=6 c/s, 14-H): ABq, 6.45, 5.86 (J=3 c/s, 12-H, 11-H); 5.00 (d, J=1 c/s, 2-H); 4.78 (m, 3-H).

Tutin-isonorketone (XIX)——To a solution of tutin-norketone (900 mg.) in MeOH (32 ml.), a solution of NaOMe (4% Na in MeOH) was added to raise pH to 7.2~7.4. After standing at room temperature for 1 hr., the solution was made slightly acidic by adding AcOH, and the solvent was distilled *in vacuo*. The residue was extracted with EtOAc, the organic layer was washed with water, and dried over $MgSO_4$. The solvent was distilled to provide a white crystalline mass which was recrystallized from acetone to yield colorless prisms, m.p. 224° (decomp.) (0.645 g.). *Anal.* Calcd. for $C_{14}H_{16}O_7$: C, 56.75; H, 5.44. Found: C, 56.84; H, 5.68. $[\alpha]_D^{30}$ −129.7° (c=0.686, MeOH). UV λ^{EtOH}_{max} mμ (log ε): 232 (3.99), 320 (1.71). IR ν cm^{-1}: 3430 (OH); 1753 (1775 cm^{-1} in $CHCl_3$, γ-lactone); 1665, 1640 (α,β-unsaturated ketone). $NMR^{pyridine\text{-}d_5}_{max}(\tau)$: 8.79 (1-$CH_3$), 6.89 (s, 14-H×2); 5.33 (d, J=6 c/s, 2-H); 5.04 (s, 5-H); 4.53 (d, J=4 c/s, 12-H); 4.39 (d, J=4 c/s, 11-H); 2.48 (d, J=6 c/s, 3-H). $NMR^{DMSO}_{max}(\tau)$: 5.52 (d), 4.46 (s), 4.31 (d) (OH).

Chlorohydrin (XX) from Tutin-isonorketone——a) A solution of tutin-isonorketone (50 mg.) in AcOH (8 ml.) was added to an acidic suspension of Pd-C (0.3 ml. of 5% $PdCl_2$, 60 mg. of charcoal), and the mixture was stirred in hydrogen atmosphere for 30 min. No uptake of hydrogen was observed. On evaporation of the solvent *in vacuo*, crystalline residue was obtained which was recrystallized from EtOAc to give colorless needles of (XX), m.p. 211° (decomp.)(40 mg.). *Anal.* Calcd. for $C_{14}H_{17}O_7Cl$: C, 50.53; H, 5.15. Found: C, 50.54; H, 5.39. UV λ^{MeOH}_{max} mμ (log ε): 232 (3.84). IR $\nu$$cm^{-1}$: 3350 (OH); 1755 ($\gamma$-lactone); 1670, 1640 ($\alpha,\beta$-unsaturated ketone). $NMR^{DMSO\text{-}d_6}_{max}(\tau)$: 9.07 ($CH_3$–$\overset{|}{\underset{|}{C}}$–); 7.63 ($CH_3CO$–); ABq, 6.24, 6.02 (J=12 c/s, 14-H×2); 5.72 (d, J=6 c/s, 2-H); ABq, 5.62, 5.54 (J=4 c/s, 12-H, 11-H); 2.60 (d, J=6 c/s, 3-H); 6.14 (s, 5-H).

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b) To a solution of tutin-isonorketone (54 mg.) in AcOH (10 ml.), 5 drops of conc. HCl were added, and the solution was stirred for 20 min. The solvent was distilled *in vacuo*, and the residue was recrystallized from EtOAc to provide colorless needles, m.p. 213° (decomp.), which show positive response to the Beilstein flame test (50 mg.). This product was identified with the product of a) by mixed melting point and IR comparison.

Acetyltutin-norketone (XXII)——Ozonized oxygen was conducted through the solution of acetyltutin (960 mg.) in EtOAc (50 ml.) at −70° for 8.5 hr. The resulting solution was hydrogenated over Pd-C, prepared from charcoal (1.1 g.) and 5% $PdCl_2$ solution (3.3 ml.) in MeOH (*ca.* 10 ml.), for 1 hr., to absorb one mole of hydrogen. The solvent was evaporated *in vacuo* to provide a crystalline residue. Recrystallization from $CHCl_3$ afforded colorless needles, m.p. 175° (decomp.) (756 mg.). *Anal.* Calcd. for $C_{16}H_{18}O_8$: C, 56.80; H, 5.36. Found: C, 56.66; H, 5.40. IR ν cm^{-1}: 3350, 1755 (shoulder), 1740, 1715. $NMR^{pyridine}_{max}(\tau)$: 8.28 ($CH_3$-$\overset{|}{\underset{|}{C}}$-); 7.96 ($CH_3COO$-); 7.50 ($CH_3CO$-C); ABq, 6.90, 5.82 (J=5 c/s, 14-H×2); ABq, 6.42, 5.81 (J=3 c/s, 12-H, 11-H).

Acetyltutin-isonorketone (XXI)——To a solution of acetyltutin-norketone (355 mg.) in MeOH (35 ml.), a solution of $NaOCH_3$ (4% Na in MeOH) was added to raise pH to 7.2~7.4. After standing at room temperature for 2.5 hr., the solution was made slightly acidic by adding AcOH, and the solvent was distilled *in vacuo*. The residue was extracted with $CHCl_3$, the organic layer was washed with water, and dried over $MgSO_4$. Evaporation of the solvent provided an oily residue which was crystallized from ether. Recrystallization from EtOAc-petr. ether yielded colorless needles, m.p. 176° (decomp.) (191 mg.). $NMR^{CDCl_3}_{max}(\tau)$: 7.99 (CH_3-$\overset{|}{\underset{|}{C}}$-); 7.54 ($CH_3CO$-C); 7.07 (s, 14-H×2); 4.96 (d, J=6 c/s, 2-H); 2.71 (d, J=6 c/s, 3-H).

Acetyltutin-isonorketone Chlorohydrin (XXIII)——A solution of acetyltutin-isonorketone (30 mg.) in AcOH (7 ml.) was stirred in hydrogen atmosphere with the acidic suspension of Pd-C prepared from 5% $PdCl_2$ solution (0.14 ml.) and charcoal (40 mg.). No absorption of hydrogen was observed during 2 hr. The catalyst was filtered, and the filtrate was evaporated *in vacuo* to provide colorless crystals. Recrystallization from $CHCl_3$-MeOH afforded colorless needles, m.p. 240° (decomp.) (30 mg.). *Anal.* Calcd. for $C_{16}H_{19}O_8Cl$: C, 51.36; H, 5.09. Found: C, 50.85; H, 5.14. IR ν cm^{-1}: 3450, 1753 (shoulder), 1730, 1676. $NMR^{DMSO\text{-}d_6}_{max}(\tau)$: 8.95 (1-Me); 8.13 (AcO-); 7.66 (MeCO-); 6.30 (diffused singlet, $-CH_2Cl$); 4.91 (d, J=6 c/s, 2-H); 2.49 (d, J=6 c/s, 3-H); 4.69 (s, OH); 4.08 (d, OH).

Coriamyrtin-norketone (XXIV)——Ozonized oxygen was passed through a solution of coriamyrtin (1.0 g.) in EtOAc (110 ml.) at −70° for 8 hr. The resultant solution was hydrogenated over Pd-C, prepared from 1 g. of charcoal and 3 ml. of 5% $PdCl_2$ solution in MeOH (*ca.* 10 ml.), to absorb 1 mole of hydrogen. The solvent was distilled *in vacuo* to yield a crystalline residue which was recrystallized from MeOH to give colorless crystals, m.p. 215° (decomp.) (0.92 g.). *Anal.* Calcd. for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75. Found: C, 60.07; H, 6.01. $[\alpha]_D^{22}$ −13.2° (c=1.21, EtOH). UV λ^{MeOH}_{max} mμ (log ε): 270 (1.45). IR ν cm^{-1}: 3400 (OH); 1775 (γ-lactone); 1709 (ketone). $NMR^{pyridine}_{max}(\tau)$: 8.54 (1-Me); 7.54 (MeCO-); ABq, 6.94, 6.70 (J=4 c/s, 14-H×2); ABq, 6.41, 5.93 (J=3 c/s, 12-H, 11-H); 4.93 (m, 3-H).

Coriamyrtin-isonorketone (XXV)——To a solution of coriamyrtin-norketone (710 mg.) in MeOH (40 ml.), a solution of NaOMe in MeOH was added to raise pH to 7.5~7.6. After standing at room temperature for 1 hr., the solution was made slightly acidic by adding AcOH, and the solvent was distilled *in vacuo*. The residue was taken up with H_2O, and extracted with EtOAc. The dried organic layer was distilled to yield a residue which was crystallized from EtOAc to give colorless needles, m.p. 153° (decomp.) (635 mg.). *Anal.* Calcd. for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75. Found: C, 59.61; H, 5.88. $[\alpha]_D^{33}$ −5.3° (c=0.94, EtOH). UV λ^{EtOH}_{max} mμ (log ε): 232 (3.93), 314 (1.65). IR ν cm^{-1}: 3380 (OH); 1755 (γ-lactone); 1673, 1643 (α,β-unsaturated ketone). $NMR^{pyridine\text{-}d_5}_{max}(\tau)$: 8.86 (Me-$\overset{|}{\underset{|}{C}}$-); 7.66 (MeCO-); ABq, 7.12, 7.03 (J=5 c/s, 14-H×2); ABq, 5.05 4.64 (J=4 c/s, 12-H, 11-H); 5.02 (s, 5-H); 2.6~2.9 (3-H, overlapped by the solvent protons).

Chlorohydrin (XXVI) from Coriamyrtin-isonorketone——a) A solution of coriamyrtin-isonorketone (XXVI) (40 mg.) in AcOH (10 ml.) was stirred for 25 min. in hydrogen atmosphere with the acidic suspension of Pd-C (5% $PdCl_2$ 0.23 ml., charcoal 60 mg.). Distillation of the solvent *in vacuo* provided a residue which was passed through a column of Al_2O_3 to give colorless crystals. Recrystallization from MeOH-petr. benzine afforded colorless prisms of (XXVI), m.p. 170~171° (27 mg.). *Anal.* Calcd. for $C_{14}H_{17}O_6Cl$: C, 53.09; H, 5.41. Found: C, 53.26; H, 5.70. UV λ^{MeOH}_{max} mμ (log ε): 231 (3.92). IR ν cm^{-1}: 3350, 1750, 1660. NMR $^{DMSO\text{-}d_6}_{max}(\tau)$: 9.00 (Me-$\overset{|}{\underset{|}{C}}$-); 7.66 (MeCO-); 6.23 (s, 14-H×2); ABq, 5.95, 5.43 (J=5 c/s, 12-H, 11-H); 2.68 (q, 3-H). $NMR^{DMSO\text{-}d_6}_{max}(\tau)$: 5.30 (s), 5.01 (s), 4.20 (d) (OH).

b) A solution of coriamyrtin-isonorketone (30 mg.) in AcOH (7 ml.) containing 3 drops of conc. HCl was stirred *in vacuo* to give a colorless oily residue which was dissolved in $CHCl_3$ and passed through a column of alumina. The crystalline residue obtained on evaporation of the solvent from the eluate was recrystallized from MeOH-petr. benzine to provide colorless prisms, m.p. 172~173° (27mg.), which showed positive response to Beilstein flame test. This product was identified with (XXVI) produced in a).

Methanolysis of Tutin-isonorketone——Tutin-isonorketone (XIX) (630 mg.) was dissolved in MeOH (30 ml.), and 60% $HClO_4$ (0.24 ml.) was added. After standing at room temperature for 18 hr., the solution was

neutralized with anhydrous K_2CO_3, and the solvent was distilled *in vacuo*. The residue was taken up with H_2O, and extracted with EtOAc. The EtOAc solution was washed with H_2O, dried over $MgSO_4$, and the solvent was distilled to yield a white crystalline mass (614 mg.). Recrystallizing from EtOH, colorless needles of (XXVII), m.p. 246° (decomp.) were obtained. *Anal.* Calcd. for $C_{15}H_{20}O_8$: C, 54.87; H, 6.14. Found: C, 55.04; H, 6.40. $[\alpha]_D^{33}$ −48.39° (c=0.73, MeOH). UV λ_{max}^{MeOH} mμ (log ε): 232 (3.86). IR ν cm^{-1}: 3400 (OH); 1760 (γ-lactone); 1668, 1640 (α,β-unsaturated ketone). $NMR_{max}^{DMSO\text{-}d_6}(\tau)$: 9.11 (Me-$\overset{|}{\underset{|}{C}}$-); 7.66 (MeCO-); 6.70 (MeO-); ABq, 6.59, 6.32 (J=11 c/s, 14-H×2); two doublets, 5.78 (J=6 c/s, 2-H), 2.61 (J=6 c/s, 3-H), which were confirmed by the NMDR technic to be mutually spin-coupled. $NMR_{max}^{DMSO}(\tau)$: 5.87 (s), 5.26 (s), 4.74 (d), 4.52 (d) (OH).

Methanolysis of Coriamyrtin-isonorketone——To a solution of coriamyrtin-isonorketone (XXV) (300 mg.) in MeOH (30 ml.), 60% $HClO_4$ (0.02 ml.) was added. After standing at room temperature for 14 hr., the solution was neutralized with K_2CO_3, filtered, and the solvent was distilled *in vacuo* to provide a white crystalline residue. Water was added to this residue, and insoluble material was filtered. The filtrated was concentrated *in vacuo* to yield colorless crystals of (XXVIII), m.p. 163~165° (258 mg.). By recrystallization from EtOAc-petr. benzine, m.p. was elevated to 166~167°. *Anal.* Calcd. for $C_{15}H_{20}O_7 \cdot H_2O$: C, 54.54; H, 6.71. Found: C, 54.83; H, 6.72. $[\alpha]_D^{30}$ +31.31° (c=1.06, MeOH). UV λ_{max}^{EtOH} mμ (log ε): 232 (3.94). IR ν cm^{-1}: 3450, 3370, 1745, 1660, 1643. $NMR_{max}^{DMSO\text{-}d_6}(\tau)$; 9.08 (Me-$\overset{|}{\underset{|}{C}}$-); 7.66 (MeCO-); 6.72 (MeO-); 6.63 (s, 14-H×2); 5.98 (d, J=5 c/s, 12-H); 5.43 (d, J=5 c/s, 11-H); 2.6~2.8 (q, 3-H). $NMR_{max}^{DMSO}(\tau)$: 5.57 (s), 5.19 (s), 4.50 (d) (OH).

Zinc Reduction of Tutin-isonorketone-methoxide (XXVII)——Zinc powder (3 g.) was added to a solution of (XXVI) (600 mg.) in hot AcOH (20 ml.). The mixture was refluxed for 1 hr., and diluted with EtOAc. The precipitate was filtered, and the filtrate was washed with $NaHCO_3$, and H_2O. After drying over $MgSO_4$, the solvent was distilled to yield a yellow oily residue which was taken up with $CHCl_3$. Insoluble material was filtered, and the filtrate was distilled to give a yellow oily residue which was crystallized from EtOAc. Recrystallization from EtOAc yielded colorless crystals of (XXIX), m.p. 183~185° (82 mg.). *Anal.* Calcd. for $C_{15}H_{20}O_7$: C, 57.68; H, 6.46. Found: C, 57.69; H, 6.71. $[\alpha]_D^{32}$ −3.89° (c=0.769, MeOH). UV λ_{max}^{MeOH}: 283 mμ (log ε 1.96). IR ν cm^{-1}: 3350, 1765, 1707, 1640. $NMR_{max}^{pyridine}(\tau)$: 8.54 (Me-$\overset{|}{\underset{|}{C}}$-); 7.74 (MeCO-); 6.73 (MeO-); 6.15 (s, 14-H×2); 5.98 (diffused doublet, J=6 c/s, 4-H); 5.68 (d, J=6 c/s, 12-H); 4.70 (d, J=6 c/s, 11-H); 3.90 (q, J_1=10 c/s, J_2=6 c/s, 3-H), 3.52 (d, J=10 c/s, 2-H).

Hydrogenation of Elimination Product (XXIX)——A solution of (XXIX) (38 mg.) in MeOH (10 ml.) was hydrogenated over Pd-C, prepared from charcoal (30 mg.) and 5% $PdCl_2$ (0.13 ml.), for 1 hr. to absorb one mole of hydrogen. The filtered solution was evaporated to dryness *in vacuo*, and the residue was taken up in H_2O and $CHCl_3$. The organic layer was washed with H_2O, dried over K_2CO_3, and then evaporated *in vacuo* to yield colorless crystals. Recrystallization from EtOAc afforded needles of (XXX), m.p. 141~143° (11 mg.). *Anal.* Calcd. for $C_{15}H_{22}O_7$: C, 57.31; H, 7.06. Found: C, 57.32; H, 7.27. $[\alpha]_D^{25}$ +65.7° (c=0.205, MeOH). $[\phi]_{300}^{25}$ +3,740°, $[\phi]_{258}^{25}$ −2,660° (c=0.337, MeOH). IR ν cm^{-1}: 3470, 1778, 1705. $NMR_{max}^{pyridine}(\tau)$: 8.57 (Me-$\overset{|}{\underset{|}{C}}$-); 7.69 (MeCO-); 6.82 (MeO-); 6.44 (s, 14-H×2); 6.15 (d, J=5 c/s, 5-H); 5.30 (d, J=3.5, 12-H); 4.89 (d, J=3.5 c/s, 11-H).

This product yielded a yellow 2,4-dinitrophenylhydrazone, m.p. 233° (decomp.). *Anal.* Calcd. for $C_{21}H_{26}O_{10}N_4$: C, 51.01; H, 5.30. Found: C, 51.20; H, 5.59. UV λ_{max}^{MeOH} mμ (log ε): 230 (4.11), 260 (3.93), 364 (4.24).

Zinc Reduction of Coriamyrtin-isonorketone-methoxide (XXVIII)——To a solution of (XXVIII) (100 mg.) in AcOH (10 ml.), zinc powder (1 g.) was added, and the mixture was refluxed for 30 min., and then diluted with EtOAc. The precipitate was filtered, and extracted with EtOAc. The filtrate, combined with the extract, was distilled *in vacuo* to yield an oily residue, which was dissolved in EtOAc, and washed with $NaHCO_3$ and H_2O. The dried EtOAc solution was distilled to provide a colorless oily residue which was dissolved in $CHCl_3$ and chromatographed on a column of silicic acid (10 g.). The effluent by $CHCl_3$-acetone (95:5) yielded colorless crystals. Recrystallization from EtOAc afforded needles, m.p. 140~142° (7 mg.), which were identified by mixed fusion and IR spectra, with (XXX) produced by the hydrogenation of (XXIX).

Hydrogenation of Coriamyrtin-isonorketone-methoxide (XXVIII)——The methoxide (XXVIII) (100 mg.) was hydrogenated over Pd-C prepared from 5% $PdCl_2$ (0.3 ml.) and charcoal (45 mg.) in MeOH (40 ml.), for 1 hr. to absorb 1.08 moles of hydrogen. The filtered solution was evaporated *in vacuo* to dryness, and the residue was extracted with $CHCl_3$. The $CHCl_3$ solution, washed with H_2O and dried over K_2CO_3, was distilled to provide an oily residue which was crystallized from acetone-petr. benzine. Recrystallization from EtOAc provided colorless needles, m.p. 143~145° (36 mg.). $[\alpha]_D^{30}$ +62.71° (c=0.41, MeOH). By IR comparison and mixed fusion, this product was identified with (XXX). The 2,4-dinitrophenylhydrazone, m.p. 236° (decomp.). prepared from this product, was also identical with the 2,4-dinitrophenylhydrazone of (XXX) produced by the hydrogenation of (XXIX).

Isomerization of Elimination Product (XXIX) to Coriamyrtin-isonorketone-methoxide (XXVIII)——A solution of (XXIX) (25 mg.) and NaOAc (25 mg.) in EtOH (10 ml.) was refluxed in nitrogen atmosphere for 4 hr. The solvent was evaporated *in vacuo*, and the residue was dissolved in a mixture of EtOAc and H_2O.

The organic layer was washed with H_2O, dried, and evaporated *in vacuo* to provide a yellow oily residue which crystallized on standing. Recrystallization from EtOAC provided colorless crystals, m.p. 162~163° (6 mg.). $[\alpha]_D^{29}$ +34.5° (c=0.2895, MeOH). This product was identified with (XXVIII) by IR comparison and mixed melting point.

O.R.D. Peaks and Troughs of α-Bromoisotutinone (IV) and Methyl β-Bromo-oxopicrotoxinate (XXXI) ——(IV): $[\phi]_{346}$ −4,760°, $[\phi]_{334}$ −3,470°, $[\phi]_{300}$ +1,710° (c=0.374, dioxane). (XXXI): $[\phi]_{346}$ −5,480°, $[\phi]_{334}$ −3,850°, $[\phi]_{300}$ +2,710° (c=0.392, dioxane). (both measured at 20°).

Benzoytutin (XXXIII)——A mixture of tutin (100 mg.), C_6H_5COCl (0.08 ml.), and pyridine (2 ml.) was allowed to stand at room temperature for 2 hr., and excess of dilute HCl was added. Viscous oil was collected by decantation of the mother liquor, and left to stand to crystallize. Recrystallization from EtOH and then from EtOH-petr. benzine provided colorless needles, m.p. 182~183° (76 mg.). *Anal.* Calcd. for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.02; H, 5.55. $[\alpha]_D^{20}$ +3.5° (c=0.427, dioxane). UV λ_{max}^{EtOH} mμ (log ε): 232 (4.17), 275 (3.01), 283 (2.95). IR ν cm^{-1}: 3400 (OH); 1770 (γ-lactone); 1715, 1600 (C_6H_5CO-), 1640 (double bond). NMR$_{max}^{CDCl_3}$(τ): 8.60 (Me-$\overset{|}{C}$-); 8.02 (s), 4.88 (m) (CH_2=$\overset{|}{C}$Me); ABq, 7.01, 6.07 (J=5 c/s, 14-H×2); ABq, 6.73, 6.18 (J=3 c/s, 12-H, 11-H).

Benzoyl α-bromotutin (XXXII)——a) A mixture of α-bromotutin (45 mg.), C_6H_5COCl (0.04 ml.), and pyridine (0.4 ml.) was allowed to stand at room temperature for 1.5 hr., and then poured into ice-chilled dilute HCl. Viscous oil was collected and tritulated with EtOH. Recrystallization from EtOH afforded colorless needles, m.p. 245° (decomp.) (40 mg.). *Anal.* Calcd. for $C_{22}H_{21}O_7Br$: C, 55.36; H, 4.44. Found: C, 55.54; H, 4.37. $[\alpha]_D^{20}$ −176° (c=1.05, dioxane). IR ν cm^{-1}: 1780, 1715, 1600, 1580, 1280. NMR$_{max}^{CHCl_3}$(τ): 8.47, 8.38 (7-H×3, 10-H×3); ABq, 7.14, 6.12 (J=5 c/s, 14-H×2); 6.74, 6.27 (J=3 c/s, 12-H, 11-H); 4.83 (m, 2-H, 3-H).

b) Benzoyltutin (20 mg.) was dissolved in warm aqueous EtOH (1:1), and bromine was added until the solution had a permanent yellow color. The mixture was left standing in an ice-box, to precipitate a white crystalline mass. Recrystallization from EtOH afforded colorless needles, m.p. 242° (decomp.). By mixed melting point and IR comparison, this product was identified with the product of a).

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