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Studies on the Constituents of *Isodon trichocarpus* Kudo. II.[1] The Structures of Enmenin, Enmelol, and Ememodin

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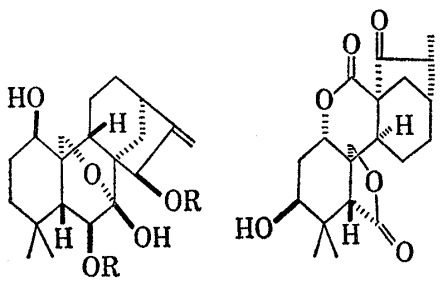
The structures of enmenin, enmelol, and ememodin, new diterpenoids isolated from *Isodon trichocarpus* Kudo were elucidated as I, II, and III, respectively.

In the previous paper,[1] we reported the structures of isodonol, enmedol, and enmenol, which are new diterpenoids having full (−)-kaurane type skeletons isolated from *Isodon trichocarpus* Kudo (Japanese name: Kurobana-hikiokoshi). Now, we wish to report the structures of three other constituents of *Isodon trichocarpus* Kudo, enmenin (compound B), enmelol (compound L), and ememodin (compound D). They also are diterpenoids, and the first two of these compounds have full (−)-kaurane type skeletons same as isodonol, but possess one less hydroxyl groups than isodonol. On the contrary, last compound has incomplete (−)-kaurane type skeleton like enmein,[3] whose structure was already established.



I R=Ac
II R=H

III

Chart 1

We propose the structures (I), (II), and (III) for enmenin, enmelol, and ememodin,[4] respectively, on the basis of the following chemical and physical data.

Structure of Enmenin

Enmenin (I), needles, mp 162—163°, has a molecular formula of $C_{24}H_{34}O_7$ (M$^+$ *m/e* 434), and its ultraviolet (UV) spectrum (in 95% EtOH) shows the absorption bands at 228.8 mμ (ε 1150) and 285 mμ (sh.) indicating the absence of ketonic group. The presence of two acetoxyl groups was obvious from its infrared (IR) spectrum (in KBr) (1735, 1725 cm^{-1}) and nuclear magnetic resonance (NMR) (D_5-pyridine) spectrum (7.96, 7.83 τ, each 3H, singlet), and in addition, the environments of two acetoxyl groups were also established from its (NMR) spectrum as IV and V. Thus, 1H singlet at 4.38 τ was assigned to H_a and 1H doublet (J=7 cps) at 4.82 τ to H_b in the partial structures (IV and V). Furthermore, the NMR spectrum (D_5-pyridine) of enmenin exhibits the presences of two tertiary methyls (9.13 and 8.87 τ, each 3H, singlet), a terminal-methylene (5.10 and 4.97 τ, each 1H, singlet), a secondary hydroxyl group >C<u>H</u>–OH (6.45 τ, 1H, singlet), a tertiary hydroxyl group >C–O<u>H</u> (6.26 τ, 1H, singlet), and

1) Part I: S. Mori, K. Shudo, T. Ageta, T. Koizumi, and T. Okamoto, *Chem. Pharm. Bull.* (Tokyo), **18**, 871 (1970).
2) Location: *Hongo 7-3-1, Bunkyo-ku, Tokyo, 113, Japan.*
3) T. Kubota, T. Matsuura, T. Tsutsui, S. Uyeo, M. Takahashi, H. Irie, A. Numata, T. Fujita, T. Okamoto, M. Natsume, Y. Kawazoe, K. Shudo, T. Ikeda, M. Tomoeda, S. Kanatomo, T. Kosuge, and K. Adachi, *Tetrahedron Letters*, **1964**, 1243.
4) The authors reported the structures of enmenin, enmelol, and ememodin as I, II, and III, respectively, at the 24th Annual Meeting of Pharmaceutical Society of Japan, Kyoto, April 1967 (Abstracts of Papers, p. 459). Independently, E. Fujita, *et al.* reported the structure of trichokaurin as I, which is identical with enmenin (*Chem. Commun.*, **1967**, 148).

ether-methylene $-CH_2-O-$ (6.09 τ, 2H, singlet). Treatment of enmenin with acetic anhydride-pyridine afforded enmenin monoacetate (VI), while oxidation with chromium trioxide–pyridine complex gave dehydroenmenin (VII). Existence of a secondary hydroxyl group was confirmed by the obove observation. Catalytic hydrogenation of enmenin over platinum afforded dihydroenmenin (VIII), in whose NMR spectrum ($CDCl_3$) 3H doublet (J=7 cps) at 9.20 τ and 1H doublet (J=10 cps) at 4.75 τ were newly produced at the expense of each 1H signal at 5.10, 4.97, and 4.38 τ, recognized in the NMR spectrum of enmenin. This fact is well interpreted, assuming the partial structure (IX) for enmenin. Thus, the newly produced methyl group of dihydroenmenin (VII) was assigned as *cis* to acetoxyl group as shown in X from the coupling constant J_{HaHb}=10 cps. Dihydroenmenin (VIII) afforded a monoacetate (XI) and dehydrodihydroenmenin (XII) by acetylation with acetic anhydride–pyridine and oxidation with chromium trioxide–pyridine complex, respectively, as in the case of enmenin itself.

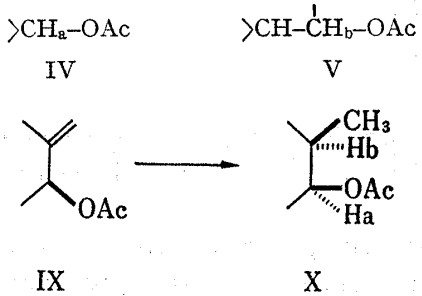
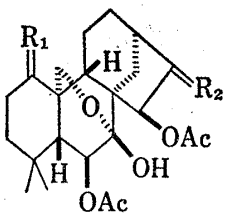


Chart 2



VI : R_1=  , R_2= 

VII : R_1=O, R_2= 

VIII : R_1=  , R_2= 

XI : R_1=  , R_2= 

XII : R_1=O, R_2= 

Chart 3

Aforementioned observation leads to the conclusion that enmenin is pentacyclic and probably has a tentative structure of XIII if we consider the structural resemblance with enmein, and assume (−)-kaurane type skeleton for enmenin. Orientation of C-6-H was assumed to be α from the coupling constant $J_{H_5H_6}$=5—7 cps[5] in the NMR spectra of enmenin derivatives.

The basic carbon skeleton was proved in the following way. Mesylation of dihydroenmenin (VIII) with methanesulfonyl chloride-pyridine afforded dihydroenmenin monomesylate (XV). The mesylate (XV) was treated with lithium aluminum hydride in ether–dioxan to give a demesylated triol (XVI) as the main product, which was identical with an authentic sample[2] obtained by acyloin condensation of enmein derivative (XIX). In addition, the fact that enmenin having the partial structures of IV and IX is recovered by sodium periodate–acetic acid treatment, establishes the partial structure of XIV.

The position and configuration of the remaining hydroxyl group was determined from the following data. The 2H singlet signal due to $-CH_2O-$ in the NMR spectrum of enmenin appears as an AB-type quartet signal (6.00 and 5.65 τ, each 1H, doublet, J=10 cps) in the NMR spectrum ($CDCl_3$) of epienmenin (XX), which was obtained by the sodium borohydride reduction of VII. This fact suggests that the hydroxyl function is situated very close to the methylene group. Besides, in the NMR spectrum ($CDCl_3$) of dehydroenmenin (VII) and dehydrodihydroenmenin (XII), the higher field doublet[6] of AB-type quartet due to $-CH_2O-$

5) See reference 14 in the previous paper *Chem. Pharm. Bull.* (Tokyo), **18**, 871 (1970). The situation is quite the same with that mentioned in this reference.

6) This higher field doublet, originating from one of the two methylene protons, is under the influence of anisotropic effect of the carbonyl group.

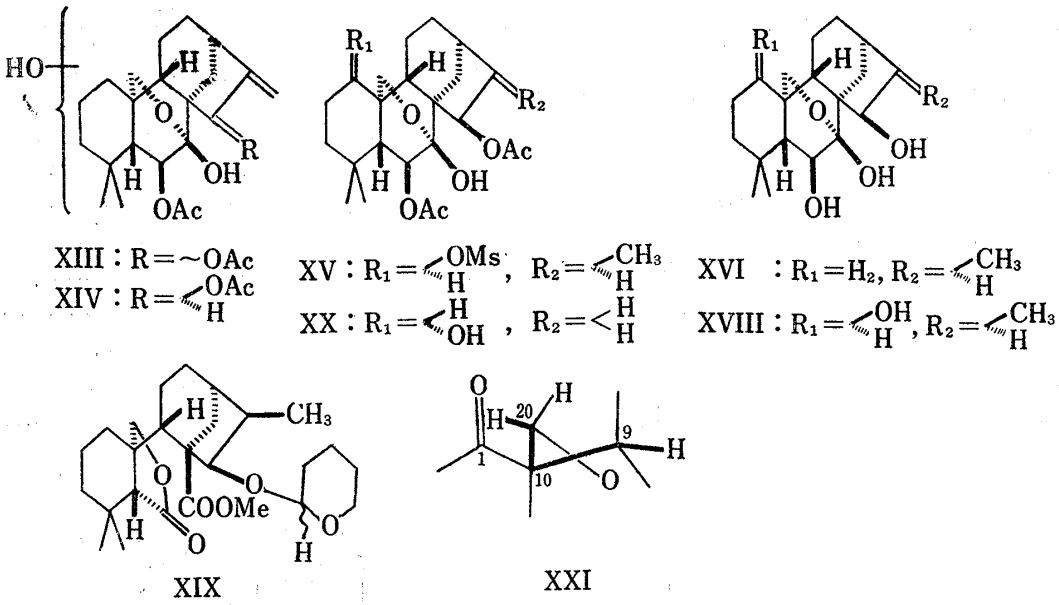


Chart 4

appears as a doublet of doublets or two broad singlets by the long range coupling between C-9-H,[7] which means that the carbonyl group exists at C-1 position and the environment of the methylene group is that shown in XXI.

Concerning the configuration of C-1-OH in enmenin, there are three observations which support β-orientation. First, enmenin (I) was adsorbed more strongly than epienmenin (XX) (C-1 epimer of enmenin) on silica gel and alumina thin-layer plates. Second, in the sodium borohydride reduction of dehydroenmenin, I and XX were produced in 1:3 yield. Third, in the NMR spectrum of enmelol (II), into which enmenin was converted without any change concerning the configuration of C-1-OH, C-1-H appears as a broad singlet. This means that C-1-H nearly bisects the neighboring two C-2 protons and C-1-OH is β-oriented.

Thus, enmenin has a structure expressed as I. Additionally, the tetraol (XVIII) obtained as a minor product in desulfurization reaction of dihydroenmenin monomesylate (XV) was also gained by treatment of dihydroenmenin (VIII) with lithium aluminum hydride represented by the structure of XVIII.

Structure of Enmelol

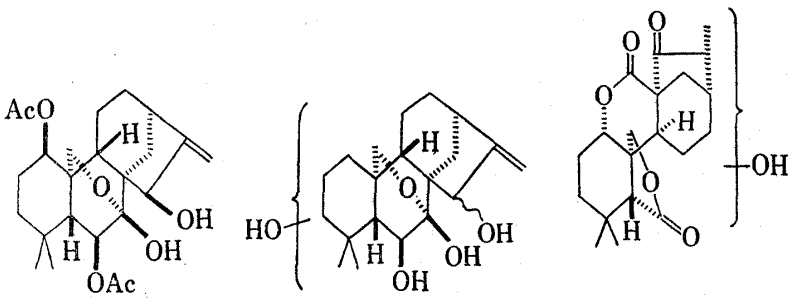
Enmelol (II), prisms, mp 263—265°, has a molecular formula of $C_{20}H_{30}O_5$ (M^+ *m/e* 350). Its NMR spectrum D_5-pyridine shows the presence of two tertiary methyls (8.87 τ, 6H, singlet), three secondary hydroxyl groups >C<u>H</u>–OH (6.30 τ, br. singlet), >CH–C<u>H</u>–OH (5.73 τ, doublet, J=5 cps), >C<u>H</u>–OH (4.83 τ, br. singlet), an *exo*-methylene (4.83, 4.55 τ, each 1H, singlet) and $-CH_2O-$ (5.93 τ, 2H, br. singlet). Absence of a carbonyl group was deduced from its IR spectrum (KBr).

Enmelol consumed 1 mole of sodium periodate, but its diacetate (XXII) did not. This fact indicates that enmelol has vicinal diols and at least one of which is acetylatable. This observation is similar to that found in enmenol.[2] If, here again, (—)-kaurane type skeleton is assumed for enmelol, it will be best represented by the structure of XXIII. This presumption was proved by the correlation between enmelol and enmenin, which was hydrogenated with lithium aluminum hydride in tetrahydrofurane to enmelol. Consequently, enmelol has the structure of II.

7) Long range coupling through σ-bond, (N.S. Bhacca and D.H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, 1964, p. 115.

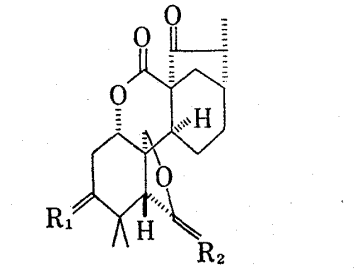
Structure of Ememodin

Ememodin (III), needles, mp 237—239°, has the same molecular formula $C_{20}H_{26}O_6$ as enmein.[3] Its IR spectrum (KBr) exhibits the presence of γ-lactone carbonyl (1777 cm^{-1}), γ-ketone carbonyl (1760 cm^{-1}), and δ-lactone or ester carbonyl (1711 cm^{-1}), while its NMR spectrum (D_5-pyridine) shows two tertiary methyls (8.90, 8.52 τ, each 3H, singlet), one secondary methyl (9.00 τ, 3H, doublet, J=6 cps), $-\underline{C}H-COO-$ (7.18 τ, 1H, singlet), $-CH_2O-$ (5.70, 5.39 τ, each 1H, doublet, J=10 cps), $>CHOH$ (6.15 τ, 1H, br. singlet), and $>\underline{C}HO-$ (4.75 τ, 1H, quartet, J=7 and 9 cps). Ememodin was recovered by the catalytic hydrogenation. From these data, we can expect enmein-type carbon skeleton (XXIV) for ememodin. If this was true, the position and configuration of the remaining secondary hydroxyl group would be C-3β-OH from the broad singlet signal at 6.15 τ attributable to the foot proton,[8] and the structure of III should be the most preferable for ememodin. This expectation was fully satisfied by the fact that ememodin was identical with the authentic sample of dihydrodehydroenmein, which is one of the two products obtained by chromium trioxide-acetic acid oxidation of dihydroenmein (XXV). Naturally, dehydroememodin (XXVI) coincided with dihydrobisdehydroenmein, which was the other oxidation product of dihydroenmein. Thus, ememodin is represented by the structure of III.



XXII XXIII XXIV

Chart 5



III : R_1 =  , R_2 = =O

XXV : R_1, R_2 = 

XXVI : R_1, R_2 = =O

Chart 6

Experimental[9]

Enmenin (I)——Enmenin was recrystallized from ether-hexane as needles, mp 162—163°. $[\alpha]_D$ −84° (c=1.012×10^{-1}, 95% EtOH). UV $\lambda_{max}^{95\%\ EtOH}$ 289 mμ (ε 1150), 285 mμ (sh.). IR ν_{max}^{KBr} cm^{-1}: 3600—3400, 1735, 1725, 1255. NMR τ (D_5-pyridine): 9.13, 8.87 (each 3H, singlet), 7.96, 7.83 (each 3H, singlet, $-OCOC\underline{H}_3\times2$), 6.45 (1H, singlet, C-1α-H), 6.26 (1H, singlet, $>O\underline{H}$), 6.09 (2H, singlet, C-20-H×2), 5.10, 4.97 (each 1H, singlet, $=\langle\underline{H}\rangle$), 4.82 (1H, doublet, J=7 cps, C-6α-H), 4.38 (1H, C-15α-H). Mass M^+ m/e 434. *Anal.* Calcd. for $C_{24}H_{34}O_7$: C, 66.34; H, 7.89. Found: C, 65.74; H, 7.86.

Enmenin Monoacetate (VI)——A solution of I (106 mg) in pyridine (2 ml) and Ac_2O (1 ml) was allowed to stand over night at room temperature. Evaporation of the solvent gave a crystalline precipitate, which was recrystallized from ether-hexane to VI (67 mg) as plates, mp 185—188°. IR ν_{max}^{KBr} cm^{-1}: 3500, 1736 (br.), 1660 (br.). NMR τ: ($CDCl_3$) 9.10, 8.85 (each 3H, singlet), 7.93, 7.90, 7.80 (each 3H, singlet, $-OCOC\underline{H}_3\times3$), 5.35 (1H, br. singlet), 5.04 (1H, br. singlet), 4.92 (1H, br. singlet), 4.74 (1H, doublet, J=7 cps, C-6α-H), 4.30 (1H, C-15α-H). *Anal.* Calcd. for $C_{26}H_{36}O_8$: C, 65.53; H, 7.61. Found: C, 65.08; H, 7.45.

Dehydroenmenin (VII)——To a solution of I (90 mg) in pyridine (1 ml), a slurry of CrO_3 (90 mg)-pyridine (4 ml) was added. The mixture was left over night at room temperature. The solvent was evaporated *in vacuo* and the residue was extracted with CH_2Cl_2. The extract was washed with water, dried over anhyd. Na_2SO_4, and chromatographed on silica gel to give a solid, which was recrystallized from acetone–hexane to VII (40 mg) as prisms, mp188—189°. UV: endo-absorption. ORD (c=0.966×10^{-1}, 95% EtOH)

8) In the NMR spectrum of enmein derivatives C-3α-H appeared as a broad singlet.

9) All melting points were measured by Yanagimoto's Micro-Melting Point Apparatus and are not corrected.

$[M]^{31}$ (mμ): 3980 (315) (peak), −5760 (275) (trough). IR ν_{max}^{KBr} cm^{-1}: 3460, 1737, 1700. NMR τ ($CDCl_3$): 9.10, 9.03 (each 3H, singlet), 7.95, 7.77 (each 3H, singlet), 6.48 (1H, singlet), 6.03, 5.64 (each 1H, singlet, $=\langle\underline{H}\rangle$), 4.88 (1H, doublet, $J=9$ cps), 4.35 (1H, C-15α-H). *Anal.* Calcd. for $C_{24}H_{32}O_7$: C, 66.65; H, 7.46. Found: C, 66.74; H, 7.36. Mass Calcd. for $C_{24}H_{32}O_7$: 432. Found: M^+ *m/e* 432.

Dihydroenmenin (VIII)——Enmenin (I) (458 mg) in MeOH (10 ml) was hydrogenated in the presence of PtO_2 (50 mg). Treatment in a usual manner gave VIII quantitatively. Crude VIII was recrystallized from MeOH to needles, mp 210—213°. IR ν_{max}^{KBr} cm^{-1}: 3540, 3430, 1737, 1713. NMR τ ($CDCl_3$): 9.20 (3H, doublet, $J=7$ cps), 9.13, 8.85 (each 3H, singlet), 7.97, 7.83 (each 3H, singlet), 6.08 (2H, singlet), 6.1 region (1H), 4.88 (1H, doublet, $J=7$ cps, C-6α-H), 4.75 (1H, doublet, $J=10$ cps, C-15α-H). *Anal.* Calcd. for $C_{24}H_{36}O_7$: C, 66.03; H, 8.31. Found: C, 65.44; H, 7.92.

Dihydroenmenin Monoacetate (XI)——To a solution of VIII (40 mg) in pyridine (2 ml), Ac_2O (2 ml) was added, and the mixture was left overnight at room temperature. The reaction mixture was concentrated under reduced pressure to give a solid, recrystallization from hexane–acetone afforded XI (30 mg) as needles, mp 165—167°. IR ν_{max}^{KBr} cm^{-1}: 3480, 1742, 1716, 1250. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550, 1735, 1250. NMR τ (CCl_4): 9.25 (3H, doublet, $J=7$ cps), 9.20, 8.86 (each 3H, singlet), 6.17 (2H), 6.17 (1H), 5.50 (1H, br. singlet), 4.98 (1H, doublet, $J=6$ cps), 4.90 (1H, doublet, $J=10$ cps, C-15α-H). *Anal.* Calcd. for $C_{26}H_{38}O_8$: C, 65.25; H, 8.00. Found: C, 65.85; H, 8.02.

Dehydrodihydroenmenin (XII)——To a solution of VIII (79 mg) in pyridine (1 ml), CrO_3 (90 mg) pyridine (4 ml) complex was added and the mixture was allowed to stand for 3 days at room temperature. After evaporation of the solvent *in vacuo*, and dilution of the residue with water, the residue was extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhyd. Na_2SO_4, and chromatographed on silica gel to afford crude XII (50 mg) as prisms. A part of crude XII was recrystallized from hexane–EtOAc to show mp 177—178°. UV: end-absorption. IR ν_{max}^{KBr} cm^{-1}: 3400, 1740, 1695, 1240. *Anal.* Calcd. for $C_{24}H_{34}O_7$: C, 66.34; H, 7.89. Found: C, 66.87; H, 8.05.

Dihydroenmenin Monomesylate (XV)——A solution of VIII (113 mg) and MsCl (1 ml) in pyridine (3 ml) was allowed to stand overnight in an ice box. After evaporation of the solvent *in vacuo*, the mixture was diluted with water, and extracted with $CHCl_3$. The extract was dried over anhyd. Na_2SO_4 and evaporated to leave a thick oil, which crystallized from hexane–EtOAc to afford XV (71 mg) as needles, mp 171—172°. IR ν_{max}^{KBr} cm^{-1}: 3460, 1745, 1715. *Anal.* Calcd. for $C_{25}H_{38}O_9S$: C, 58.35; H, 7.44. Found: C, 58.80; H, 7.51.

Demesylation of XV——A solution of XV (97 mg) in ether (10 ml)–dioxane (4 ml) was treated with $LiAlH_4$ (140 mg) under stirring for 7 hr at room temperature. After destruction of excess reagent with 2N HCl, the reaction mixture was extracted with EtOAc. The extract was washed with water, dried over Na_2SO_4, and evaporation of EtOAc gave an oil (75 mg), which was chromatographed on silica gel column. Elution with CH_2Cl_2–EtOAc (4:1) gave three kinds of products, which were demesylated triol (XVI) (11 mg), a by-product (XVII) (trace), and hydrolyzed tetrol (XVIII) (5.8 mg). The triol (XVI) was recrystallized from EtOAc as needles, mp 207—210°. $[\alpha]_D^{14}$ −53° ($c=0.755\times10^{-1}$, 95% EtOH). IR ν_{max}^{KBr} cm^{-1}: 3460, 3400, 1165, 1080, 1060. NMR τ (D_5-py.): 8.93, 8.86 (each 3H, singlet), 8.82 (3H, doublet, $J=7$ cps), 8.55 (1H, doublet, $J=5$ cps), 7.6 (1H, multiplet), 6.01 (2H, AB-type, quartet, $J=10$ cps), 5.9 (1H, doublet, $J=5$ cps, C-6α-H), 5.12 (1H, doublet, $J=10$ cps, C-15α-H). *Anal.* Calcd. for $C_{20}H_{32}O_4$: C, 71.39; H, 9.59. Found: C, 71.73; H, 9.66. Mass Calcd. for $C_{20}H_{32}O_4$: 336. Found: M^+ *m/e* 336.

The triol (XVI) obtained as above was identical with an authentic sample obtained by acyloin condensation of XIX[7] by mixed mp, IR, and $[\alpha]_D$. The tetrol (XVIII) (prisms), mp 218—221°, was identical with the hydrolysis product of VIII.

Hydrogenolysis of VIII to XVIII——i) A solution of VIII (193 mg) in dioxane (25 ml) was treated with $LiAlH_4$ (60 mg) under stirring for 70 hr at room temperature. The reaction mixture was acidified with 2N HCl and extracted with EtOAc. Evaporation of EtOAc and recrystallization of the residue gave XVIII (31 mg) as prisms, mp 220—223°, which consumed 1 mole of periodate IR ν_{max}^{KBr} 3320 cm^{-1}. *Anal.* Calcd. for $C_{20}H_{32}O_5$: C, 68.15; H, 9.15. Found: C, 68.20; H, 9.06. Mass Calcd. for $C_{20}H_{32}O_5$: 352. Found: M^+ *m/e* 352.

ii) VIII (132 mg) in MeOH (6 ml) was hydrolyzed with 5% $NaHCO_3$ (6 ml) under reflux for 3.5 hr. Extraction of the products with EtOAc, washed with water, dried, and concentrated to give needles (9.2 mg), mp 239—241°, which consumed 1 mole of periodate and was considered to be XVIII containing 1 mole of H_2O. Mass M^+ *m/e* 352. *Anal.* Calcd. for $C_{20}H_{32}O_5\cdot H_2O$: C, 64.86; H, 9.19. Found: C, 64.67; H, 8.69.

$NaBH_4$ Reduction of VII——A mixture of VII (41 mg) and $NaBH_4$ (50 mg) in MeOH (5 ml) was left standing for 3 hr. The reaction mixture was diluted with water, extracted with CH_2Cl_2, and dried and evaporation of CH_2Cl_2 *in vacuo* gave an amorphous residue (27 mg), which was chromatographed on silica gel. Elution with $CHCl_3$ gave two kinds of products. One was enmenin (5.5 mg) and the other was epienmenin (XX) (14.6 mg), which was recrystallized from hexane–EtOAc to show mp 199—201°. IR ν_{max}^{KBr} cm^{-1}: 3460, 1730, 1252. NMR τ ($CDCl_3$): 9.18, 8.88 (each 3H, singlet), 7.99, 7.78 (each 3H, singlet, $-OCOCH_3\times2$),

6.3—6.5 (2H) 6.03, 5.75 (each 1H, doublet, $J=10$ cps, C-20-H×2), 5.15, 5.00 (each 1H, singlet, $=\langle\frac{H}{H}\rangle$), 4.87 (1H, doublet, $J=7.5$ cps, C-6α-H), 4.4 (1H, C-15α-H).

Enmelol (II)——Enmelol was recrystallized from EtOAc as prisms, mp 263—265°, which consumed 1 mole of periodate. $[\alpha]_D^{35}$ −48 ($c=0.836\times10^{-1}$, 95% EtOH). IR ν_{max}^{KBr} cm^{-1}: 3520, 3300. NMR (D_5-py.): 8.87 (6H, singlet), 7.0 (1H), 6.30 (1H, br. singlet), 5.93 (2H, br. singlet), 5.73 (1H, doublet, $J=5$ cps, C-6α-H), 4.83, 4.55 (each 1H, singlet, $=\langle\frac{H}{H}\rangle$), 4.83 (1H, singlet). *Anal.* Calcd. for $C_{20}H_{30}O_5$: C, 68.54; H, 8.63. Found: C, 68.65; H, 8.87. Massc alcd. for $C_{20}H_{30}O_5$: 350. Found: M^+ *m/e* 350.

Enmelol Diacetate (XXII)——Enmelol (II) (17 mg) in pyridine (1 ml) was treated with Ac_2O (1 ml) for 66 hr at room temperature. The reaction mixture was concentrated and the residue was chromatographed on silica gel to give an oily XXII (17.5 mg), which did not consume periodate. NMR τ (CCl_4): 9.12, 8.84 (3H, singlet), 7.96, 7.85 (3H, singlet), 6.1 (2H, singlet).

Hydrogenolysis of I to II——A mixture of I (80 mg) and $LiAlH_4$ (100 mg) in THF (6 ml) was left to stand for 13 hr at room temperature. The reaction mixture was acidified with dil. HCl and extracted with EtOAc. The extract was dried over anhyd. Na_2SO_4 and evaporation of EtOAc gave a crystalline precipitate, whose recrystallization from EtOAc afforded II as prisms (22 mg), mp 259—261°, which was identical with an authentic sample by mixed mp, IR, and $[\alpha]_D$.

Ememodin (III)——Ememodin was recrystallized from MeOH as needles, mp 237—239°. $[\alpha]_D^{17}$ −131° ($c=0.498\times10^{-1}$, 95% EtOH). IR ν_{max}^{KBr} cm^{-1}: 3480, 1777, 1760, 1711. NMR τ (py.): 9.00 (3H, doublet, $J=6$ cps), 8.90, 8.52 (each 3H, singlet), 7.18 (1H, singlet, C-5α-H), 6.15 (1H, br. singlet, C-3α-H), 5.70, 5.39 (each 1H, doublet, $J=10$ cps, C-20-H×2), 4.75 (1H, quartet, $J=7$ and 9 cps). *Anal.* Calcd. for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 66.12; H, 7.09. III was identified with dihydrodehydroenmein by mixed mp and IR.

Dehydroememodin (XXVI)——To a solution of III (99 mg) in AcOH (3 ml), CrO_3 (100 mg) was added and the mixture was left over night at room temperature. The reaction mixture was concentrated under reduced pressure, diluted with water, and extracted with $CHCl_3$. The organic layer was washed with water, dried, and evaporated to give crude XXVI (68 mg) as a solid. Its recrystallization from acetone afforded fine needles, mp 221—222.5°. IR ν_{max}^{KBr} cm^{-1}: 1782, 1762, 1725. Dehydroememodin was identical with dihydrobisdehydroenmein by mixed mp and IR.

Acknowledgement The authors are grateful to the members of Central Analysis Room of the Faculty for elemental analysis and spectral data.