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181. Hiroshi Hikino, Yasuko Hikino, and Tsunematsu Takemoto : Structure and Absolute Configuration of Kanokonol.*1

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Kanokonol is the sesquiterpenoid keto-alcohol which has been found in several kinds of Japanese valerian.[1~3] In a preliminary communication,[4] we ascribed stereostructure I (R=H) to kanokonol; this paper presents the evidence in full detail.

Kanokonol occurs mainly as its oily acetate (I; R=Ac) whose infrared spectrum shows the presence of an acetoxyl (1740 cm^{-1}), a ketonic carbonyl in a six-membered or larger ring (1702 cm^{-1}), and a methylene adjacent to carbonyl (1425 cm^{-1}). On hydrolysis, the acetate (I; R=Ac) gave the crystalline keto-alcohol (I; R=H), kanokonol, the infrared spectrum of which exhibits a hydroxyl band (3515 cm^{-1}), a ketonic carbonyl band (1692 cm^{-1}), and an active methylene band (1414 cm^{-1}). The ketol (I; R=H) was also characterized as its semicarbazone. The nuclear magnetic resonance spectra of the ketol (I; R=H) and its acetate (I; R=Ac) disclose the presence of two doublet methyls, one unsplit methyl, and one hydroxy- or acetoxy-methylene as a quartet in an AB system. The latter indicates that the methylene is attached to a fully-substituted carbon atom and that rotation about the bond between the methylenic carbon and the quarternary carbon is restricted. The existence of these functions and the molecular formula $C_{15}H_{26}O_2$ require kanokonol to be a saturated bicyclic compound.

The relative situation of the hydroxyl and the carbonyl group in kanokonol was first taken into consideration. Oxidation of kanokonol with chromic acid yielded the carboxylic acid (II), a fact which confirmed that the alcohol is primary. The keto-acid (II) proved resistant to routine reduction with sodium borohydride. Consequently, lithium aluninum hydride reduction was carried out to give the desired hydroxy-acid (III) in which, from its infrared band at 1675 cm^{-1}, due to a chelated carbonyl, the hydroxyl group appears spatially close to the carboxyl group. Treatment with acetic anhydride afforded the lactone (IV) which has an infrared band at 1767 cm^{-1} characteristic of a γ-lactone. Hydrolysis of the lactone (IV) regenerated the hydroxy-acid (III) while reduction of the lactone (IV) with lithium aluminum hydride gave the diol (VI; R=H) (*vide infra*). These results established that kanokonol contains the partial structure -CO-C-C$\lessdot$$CH_2OH$.

Reduction of kanokonol (I; R=H) with sodium and ethanol gave the diol (V; R=H), valerane-4β,15-diol. Although the nuclear magnetic resonance spectrum of the diol (V; R=H) could not be determined because of its low solubility in a suitable solvent, in the nuclear magnetic resonance spectrum of its diacetate (V; R=Ac), a broad peak with a half-band-width of 17 c.p.s., due to the C-4 methine proton, indicates that the C-4 hydroxyl group is equatorially disposed. On reduction with lithium aluminum hydride, kanokonol (I; R=H) yielded, together with the diol (V; R=H), the epimeric diol (VI; R=H), valerane-4α,15-diol. The nuclear magnetic resonance spectra of the diol (VI; R=H) and its diacetate (VI; R=Ac) exhibit an unresolved band with a half-

*1 This paper is Part II in the series on Sesquiterpenoids. Preceding paper, Part I, H. Hikino, Y. Hikino, Y. Takeshita, K. Meguro, T. Takemoto : This Bulletin, **13**, 1408 (1965).

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1) H. Hikino, Y. Hikino, H. Kato, Y. Takeshita, T. Takemoto : Yakugaku Zasshi, **83**, 219 (1963).
2) H. Hikino, Y. Hikino, Y. Takeshita, Y. Isurugi, T. Takemoto : *Ibid.*, **83**, 555 (1963).
3) H. Hikino, Y. Hikino, T. Takeshita, H. Kato, T. Takemoto : *Ibid.*, **85**, 179 (1965).
4) H. Hikino, Y. Hikino, T. Takemoto : This Bulletin, **11**, 1210 (1963).

band-width of 6 and less than 6 c.p.s.,*3 respectively, indicating the axial orientation of the C-4 hydroxyl group. Dehydration of the diol (Ⅵ; R=H) with *p*-toluenesulfonic acid gave the oxide (Ⅶ) whose structure was confirmed by an infrared band at 1022 cm^{-1} attributed to the ether function and by a nuclear magnetic resonance multiplet (3H) in the 6.32~6.68 τ region associated with the partial structure $-CH_2-O-CH<$. In the nuclear magnetic resonance spectra of the two diacetate, Ⅴ (R=Ac) and Ⅵ (R=Ac), the same inversion of the chemical shifts (5.04 and 5.4 τ,*3 respectively) between the C-4 axial and equatorial protons was again observed as in the cases of 4-*epi*-valeranol and valeranol and their derivatives.[5] This may reflect the unusual carbon skeleton of the compounds, although the reasons for this anomaly are not clear at the moment.

The close structural relationship between kanokonol and valeranone was underlined by the following evidence. 1) The nuclear magnetic resonance spectra of kanokonol and its acetate are closely similar to that of valeranone and might well be explained if one of the tertiary methyl groups in valeranone were replaced by a

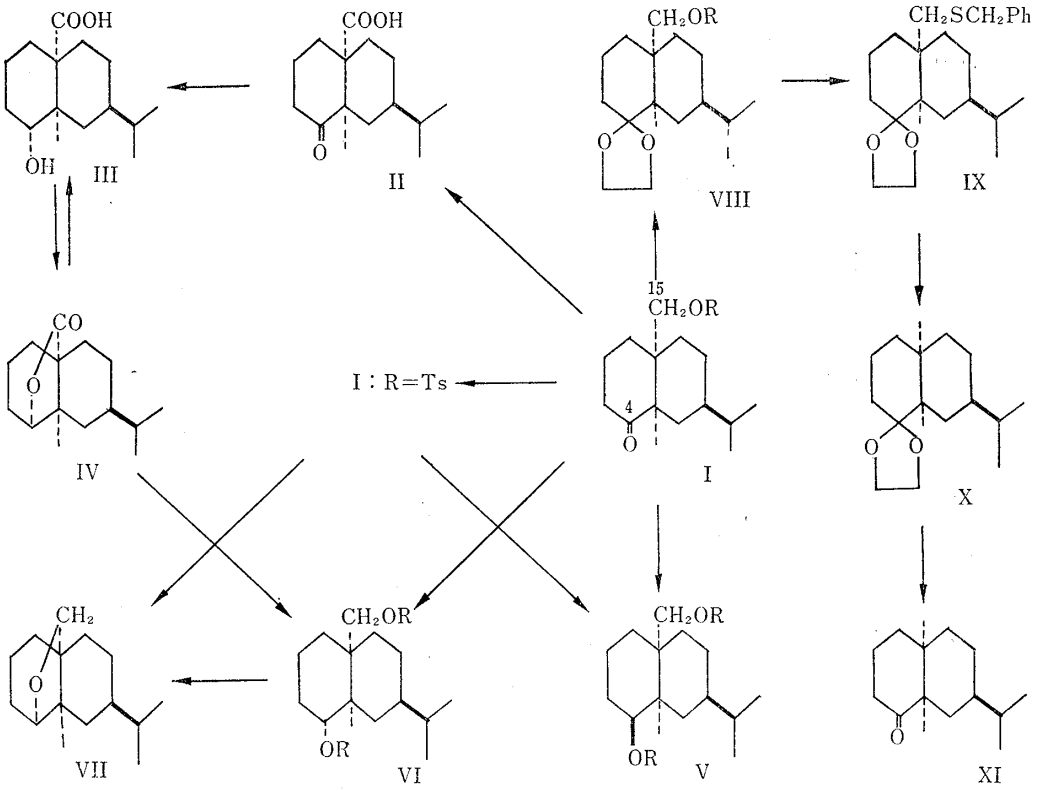

Chart 1.

hydroxymethylene grouping. 2) The optical rotatory dispersion of kanokonol gives a negative Cotton effect, the curve being almost superimposable on that of valeranone. 3) Base-catalyzed replacement of activated hydrogens in kanokonol for deuterium was carried out evaluating the extent of deuterium incorporation by mass spectrometry. In the mass spectrum cracking patterns, kanokonol showed a parent mass at 238, while, after exchange, moved to 240, corresponding to the exchange of two hydrogen atoms. The infrared spectrum of the exchanged ketone, dideuteriokanokonol, no longer exhibits a band in the 1410 region (active methylene) as in kanokonol but does

*3 Overlapping of the signal with the quadruplet due to the C-15 methylene grouping does not allow exact determination.

5) H. Hikino, Y. Hikino, Y. Takeshita, K. Meguro, T. Takemoto : This Bulletin, **11**, 1207 (1963); *Ibid.*, **13**, 1408 (1965).

show a band at 2212 cm^{-1} associated with the C-D stretching frequency. These findings suggest that the carbonyl of kanokonol is located as in the part structure $-CH_2-CO-C\lessdot$; a system found also in valeranone.

The correctness of the above arguments was proved by the following series of reactions by which kanokonol was converted into valeranone. An attempt to transform the hydroxy-methylene grouping of kanokonol into a methyl group *via* its tosylate was first made. Reduction of kanokonyl tosylate (I; R=Ts) with lithium aluminum hydride gave, however, none of the expected deoxy-compound, but, instead, the oxide (Ⅶ), together with a small amount of the diol (Ⅴ; R=H). This result may be plausibly explained as described below. A part of the reduction proceeded with incipient attack of the reagent to the C-4 carbonyl group from the α-side giving the 4β-hydroxyl group and with the following cleavage of the O-S bond to yield a minute amount of the diol (Ⅴ; R=H). On the other hand, main attack must have taken place from the opposite β-side forming the 4α-axial hydroxyl followed by the desired fission of the C(15)-O bond with concomitant attack of the hydroxyl to furnish the five-membered oxide bridge. A new approach, therefore, required the protection of the C-4 carbonyl group. The ketol (I; R=H) was converted into the ethylene ketal (Ⅷ; R=H) which was tosylated and subsequently reduced by lithium aluminum hydride. However, the reduction unexpectedly proceeded with the exclusive fission of the O-S bond to regenerate the original ketal (Ⅷ; R=H). Hence, the tosylate (Ⅷ; R=Ts) was further transformed to the benzylthioether (Ⅸ) which on desulfurization by treatment with Raney nickel gave a product with properties fully compatible with those of the required deoxy-ketal (X). Removal of the protecting group of the product (X) yielded the corresponding ketone which was shown to be identical with valeranone. The structure and absolute stereochemistry of valeranone, as indicated in formula Ⅺ, have recently been elucidated by us.[5] It becomes, therefore, possible to reprsent the structure of kanokonol as 15-hydroxyvaleranone (I; R=H).

Subsequent to our preliminary communication,[4] Indian workers have isolated kanokonol*[4] from an Indian valerian[6] and, in their independent investigation, arrived at the same conclusions about its gross structure as our own, but presented no persuasive evidence about its stereochemistry.[7]

Experimental*[5]

Kanokonyl Acetate——$C_{17}H_{28}O_3$, d_4^{25} 1.050, n_D^{25} 1.490, $[\alpha]_D$ −54.2°(c=10.1), IR (liquid) cm^{-1} : 1740, 1227 (acetoxyl), 1702 (carbonyl), 1425 (methylene adjacent to carbonyl), NMR : doublet (6H) at 9.12 τ (J=5.0, $(C\underline{H}_3)_2CH$-), singlet (3H) at 8.97 τ ($C\underline{H}_3-C\lessdot CO$-), singlet (3H) at 8.08 τ ($C\underline{H}_3$-CO-O), quadruplet (2H) in an AB system at 6.12 and 6.30 τ (J=11.2, $CH_3COO-C\underline{H}_2-C\lessdot$).

Hydrolysis of Kanokonyl Acetate——A solution of kanokonyl acetate (I; R=Ac) (1.0 g.) in 2*N* ethanolic KOH (20 ml.) was heated under reflux for 1 hr. Removal of the solvent, addition of H_2O, extraction with ether, and crystallization from light petroleum yielded kanokonol (I; R=H) as colorless needles, m.p. 53~54°, $[\alpha]_D$ −71.0° (c=7.4), ORD (c=0.379, MeOH) : $[M]_{313}^{trough}$ −6330°, $[M]_{268}^{peak}$ +8570°, mol. wt. 238 (mass spec.), *Anal.* Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found : C, 75.56; H, 10.98, IR (KBr) cm^{-1} : 3515 (hydroxyl), 1692 (carbonyl), 1414 (methylene adjacent to carbonyl), NMR : doublet (6H) at 9.16 τ (J=5.0, $(C\underline{H}_3)_2CH$-), singlet (3H) at 8.99 τ ($C\underline{H}_3-C\lessdot CO$-), singlet (1H) at 7.18 τ ($\underline{H}O$-), quadruplet (2H) in an AB system at 6.62 and 6.76 τ (J=11.0, $HO-C\underline{H}_2-C\lessdot$).

*[4] The Indian authors did not adopt this name. However, the name "kanokonol" had properly been proposed in our earlier publications[1,2,4] prior to submission of their papers.[6,7]

*[5] Melting points and boiling points are uncorrected. Specific rotations were measured in $CHCl_3$ solution unless otherwise indicated. NMR spectra were determined at 60 Mc.p.s. in CCl_4 solution against internal Me_4Si unless specified to the contrary. Chemical shifts are given in τ-values and coupling constants (J) in c.p.s.

6) C. S. Narayanan, K. S. Kulkarni, A. S. Vaidys, S. Kanthamani, G. Lakshmi Kumari, B. V. Bapat, S. K. Paknikar, S. N. Kulkarni, G. R. Kelkar, S. C. Bhattacharyya : Tetrahedron, **20**, 963 (1964).
7) K. S. Kulkarni, S. K. Paknikar, S. C. Bhattacharyya : *Ibid.*, **20**, 1289 (1964).

The derived semicarbazone crystallized from acetone as colorless flat needles, m.p. 185~186°, *Anal.* Calcd. for $C_{16}H_{29}O_2N_3$: C, 65.05; H, 9.90. Found : C, 64.87; H, 10.18.

Oxidation of Kanokonol with Chromic Acid——A solution of kanokonol (350 mg.) in ether (20 ml.) was stirred with a solution of $Na_2Cr_2O_7$ (0.4 g.) in dil. H_2SO_4 (1:6; 2 ml.) at room temperature for 2.5 hr. The reaction mixture was worked up as usual and crystallization of the acidic product (281 mg.) from ether-light petroleum gave the keto-acid (Ⅱ) as colorless flat needles, m.p. 152~153°, $[\alpha]_D$ −40.6° (c=9.8), *Anal.* Calcd. for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found : C, 71.56; H, 9.66, IR (KBr) cm^{-1} : 3400~3050, 2800~2400, 1709, 1242, 936 (carboxyl), 1694 (carbonyl).

Attempted Reduction of the Keto-acid with Sodium Borohydride——The keto-acid (Ⅱ) (49 mg.) was treated with an excess of $NaBH_4$ in MeOH (15 ml.) and 2*N* NaOH (0.1 ml.) at room temperature for 2 hr. The excess of the reagent was decomposed with AcOH. Removal of the solvent, addition of H_2O, extraction with ether gave a solid which on crystallization from ether-light petroleum afforded the keto-acid (Ⅱ), m.p. 151~152°, undepressed on admixture with the starting material. The identity was also confirmed by IR comparison.

Reduction of the Keto-acid with Lithium Aluminum Hydride——The keto-acid (Ⅱ) (52 mg.) was treated with a small excess of $LiAlH_4$ in ether (15 ml.) at room temperature for 2 min. The reaction was terminated with H_2O and dil. H_2SO_4 added. When worked up in the usual way, the ethereal extraction gave a solid (46 mg.) which after repeated crystallization from AcOEt afforded the hydroxy-acid (Ⅲ) as colorless flat needles, m.p. 183~184°, $[\alpha]_D$ +58.5° (c=2.5, EtOH), *Anal.* Calcd. for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found : C, 71.01; H, 10.48, IR (KBr) cm^{-1} : 3205 (hydroxyl), 2800~2300, 1675, 1247, 950 (carboxyl).

Lactonization of the Hydroxy-acid——A solution of the hydroxy-acid (Ⅲ) (50 mg.) in Ac_2O (2 ml.) was heated under reflux for 1.5 hr. Treatment with H_2O, extraction with ether, and crystallization from light petroleum yielded the γ-lactone (Ⅳ) as colorless leaflets, m.p. 64~66°, $[\alpha]_D$ +45.8° (c=9.6), *Anal.* Calcd. for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found : C, 76.16; H, 10.28, IR (KBr) cm^{-1} : 1767 (γ-lactone).

Hydrolysis of the γ-Lactone——A solution of the lactone (Ⅳ) (20 mg.) in 2*N* ethanolic NaOH (2 ml.) was heated under reflux for 2 hr. The acidic product was crystallized from AcOEt to give the hydroxy-acid (Ⅲ), m.p. 182~184°. The identity was confirmed by mixed melting point and IR comparison.

Reduction of the γ-Lactone with Lithium Aluminum Hydride——A solution of the lactone (Ⅳ) (200 mg.) and $LiAlH_4$ (0.3 g.) in ether (20 ml.) was stirred at room temperature for 15 hr. The product was worked up in the usual manner and crystlllized from AcOEt to give valerane-4α,15-diol (Ⅵ; R=H) as colorless prisms, m.p. 120~121°. Identification with the diol (Ⅵ; R=H) obtained by $LiAlH_4$ reduction of kanokonol (*vide infra*) was carried out by mixed melting point and IR comparison.

Reduction of Kanokonol with Sodium and Ethanol——Metallic Na (0.1 g.) was gradually added to a solution of kanokonol (50 mg.) in EtOH (3 ml.) and the mixture was heated under reflux for 3 hr. Addition of H_2O and evaporation of EtOH under reduced pressure deposited a precipitate which was collected and crystallized from iso-Pr_2O to give valerane-4β,15-diol (Ⅴ; R=H) as colorless needles, m.p. 152.5~153°, $[\alpha]_D$ +34.8° (c=5.7, EtOH), *Anal.* Calcd. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found : C, 74.92; H, 11.86, IR (KBr) cm^{-1} : 3279 (hydroxyl).

The derived diacetate (Ⅴ; R=Ac) distilled as a colorless viscous oil, n_D^{25} 1.480, $[\alpha]_D$ +21.7° (c=8.8), *Anal.* Calcd. for $C_{19}H_{32}O_4$: C, 70.33; H, 9.94. Found : C, 70.39; H, 9.92, IR (liquid) cm^{-1} : 1738, 1236 (acetoxyl), NMR ($CDCl_3$) : broad peak (band width at half height : 17 c.p.s., 1H) at 5.04 τ (H-C≤OAc).

Reduction of Kanokonol with Lithium Aluminum Hydride——A mixture of kanokonol (210 mg.) and $LiAlH_4$ (50 mg.) in ether (15 ml.) was stirred at room temperature for 5 hr. The product (210 mg.) was chromatographed over alumina (50 g.).

The AcOEt eluate (51 mg.), when crystallized from iso-Pr_2O, gave valerane-4β,15-diol (Ⅴ; R=H) as colorless needles, m.p. 152~152.5°, $[\alpha]_D$ +31.4° (c=4.5, EtOH), IR (KBr) cm^{-1} : 3280 (hydroxyl). The identity was confirmed by mixed melting point and IR comparison.

The MeOH eluate (97 mg.) was crystallized from AcOEt to afford valerane-4α,15-diol (Ⅵ; R=H) as colorless prisms, m.p. 121~122°, $[\alpha]_D$ +44.0° (c=9.7), *Anal.* Calcd. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found : C, 75.01; H, 11.88, IR (KBr) cm^{-1} : 3300 (hydroxyl), NMR ($CDCl_3$) : unresolved band (band width at half height : 6 c.p.s., 1H) at 6.72 τ (H-C≤OH).

The derived diacetate (Ⅳ; R=Ac) distilled as a colorless viscous oil, n_D^{25} 1.480, $[\alpha]_D$ +12.1° (c=8.6), *Anal.* Calcd. for $C_{19}H_{32}O_4$: C, 70.33; H, 9.94. Found : C, 70.49; H, 9.99, IR (liquid) cm^{-1} : 1738, 1235 (acetoxyl), NMR ($CDCl_3$) : unresolved band (band width at half height : <6 c.p.s.,*3 1H) at *ca.* 5.4 τ*3 (H-C≤OAc).

Dehydration of Valerane-4α,15-diol——A mixture of valerane-4α,15-diol (Ⅵ; R=H) (90 mg.) and *p*-toluenesulfonic acid (70 mg.) in xylene (2 ml.) was heated under reflux for 10 min. Chromatography of the product on alumina (5 g.) in benzene and distillation of the eluate under reduced pressure gave the oxide (Ⅶ) as a colorless liquid, n_D^{25} 1.497, $[\alpha]_D$ +88.9° (c=1.7), IR (liquid) cm^{-1} : 1022 (oxide). The identity with the oxide (Ⅶ) obtained by $LiAlH_4$ reduction of kanokonyl tosylate (Ⅰ; R=Ts) (*vide infra*) was confirmed by VPC analysis and IR comparison.

Deuteration of Kanokonol——Deuterium exchange was effected by treating kanokonol (20 mg.) in *N* NaOD (1 ml.) and dioxane (1 ml.) at 100° for 10 min. After cooling, the solvent was distilled off under diminished pressure. The same sequence of experiments was repeated further three times. Extraction with ether followed by distillation *in vacuo* gave dideuteriokanokonol, mol. wt. 240 (mass spec.), IR (Nujol) cm^{-1}: 2212 (C-D), 3436 (hydroxyl), 1690 (carbonyl), no band due to a methylene adjacent to carbonyl.

Tosylation of Kanokonol——A mixture of kanokonol (350 mg.) and TsCl (1.0 g.) in pyridine (3.5 ml.) was left standing for 22 hr. The product isolated in the usual way was adsorbed on alumina (10 g.). Elution with benzene afforded the *p*-toluenesulfonate (I; R=Ts) as a viscous oil, IR (liquid) cm^{-1}: 1701 (carbonyl), 1600, 1362, 1174 (tosylate).

Reduction of Kanokonyl Tosylate with Lithium Aluminum Hydride——The *p*-toluenesulfonate (I; R=Ts) (700 mg.) was treated with an excess of $LiAlH_4$ in ether (20 ml.) at room temperature for 20 hr. The product (455 mg.) was chromatographed over silica gel (15 g.).

From the fractions eluted with light petroleum-benzene, the oxide (VII) was obtained as a colorless liquid, $b.p_5$ 118°, d_4^{25} 0.984, n_D^{25} 1.497, $[\alpha]_D$ +62.1° (c=11.2), *Anal.* Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found; C, 81.35; H, 11.94, IR (liquid) cm^{-1}: 1022 (oxide), NMR: doublet (6H) at 9.09 τ (J=5.4, $(CH_3)_2CH$-), singlet (3H) at 8.95 τ (CH_3-C<), eight lines (3H) in the 6.32~6.68 τ region (-CH_2-O-CH<).

From the fractions eluted with ether, valerane-4β,15-diol (V; R=H) was obtained as colorless needles (from iso-Pr_2O), m.p. 150~151° (identical IR spectrum).

Ketalization of Kanokonol——A mixture of kanokonol (512 mg.) and ethylene glycol (625 mg.) in benzene (20 ml.) with addition of TsOH (5 mg.) was heated under reflux for 10 hr. taking off the separated H_2O. The product (543 mg.) was chromatographed over alumina (10 g.), being eluted with benzene. After distillation under reduced pressure the ethylene ketal (VIII; R=H) was obtained as a colorless viscous liquid, $b.p_{0.06}$ 122°, n_D^{25} 1.512, $[\alpha]_D$ +11.7° (c=10.6), *Anal.* Calcd. for $C_{17}H_{30}O_3$: C, 72.30; H, 10.71. Found: C, 71.97; H, 10.51, IR (CCl_4) cm^{-1}: 3665, 3527 (hydroxyl), 1190, 1073 (ketal).

Tosylation of Kanokonol Ethylene Ketal——A mixture of the ketal (VIII; R=H) (408 mg.) and TsCl (800 mg.) in pyridine (5 ml.) was set aside at room temperature overnight and poured on crushed ice. The product in benzene was filtered through alumina (15 g.) and crystallized from light petroleum to give the *p*-toluenesulfonate (VIII; R=Ts) as colorless prisms, m.p. 88°, *Anal.* Calcd. for $C_{24}H_{36}O_5S$: C, 66.03; H, 8.31. Found: C, 66.37; H, 8.32, IR (KBr) cm^{-1}: 1600, 1350, 1174 (tosylate).

Attempted Reduction of Kanokonol Ethylene Ketal Tosylate with Lithium Aluminum Hydride——Treatment of the *p*-toluenesulfonate (VIII; R=Ts) (33 mg.) with an excess of $LiAlH_4$ in ether (10 ml.) at room temperature overnight regenerated the ketal (VIII; R=H) (identical IR spectrum).

Reaction of Kanokonol Ethylene Ketal Tosylate with Benzyl Mercaptane followed by Raney Nickel——Metallic Na (0.4 g.) was slowly added to a solution of the *p*-toluenesulfonate (VIII; R=Ts) (720 mg.) and benzyl mercaptane (1.2 g.) in diglyme (15 ml.) and the mixture was heated under reflux for 4 hr. Addition of H_2O and extraction with ether gave a gum from which excess benzyl mercaptane was removed by steam distillation. The oily product (IX), IR (liquid) cm^{-1}: 3070, 3040, 1603, 1495, 699 (phenyl), 2674, 1418 (methylene adjacent to sulfur), without further purification, was refluxed with Raney Ni (2.5 g.) in EtOH (20 ml.) for 8 hr. After isolation in the customary manner, the product was chromatographed over alumina (50 g.). Elution with light petroleum and distillation under reduced pressure afforded valeranone ethylene ketal (X) as a colorless oil, n_D^{25} 1.497, $[\alpha]_D$ +23.2° (c=10.3), *Anal.* Calcd. for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.78; H, 11.16, IR (liquid) cm^{-1}: 1198, 1078 (ketal).

Hydrolysis of Valeranone Ethylene Ketal——A solution of valeranone ketal (X) (0.2 g.) in dil. HCl, prepared from conc. HCl (1 ml.), H_2O (1 ml.), and EtOH (7 ml.), was heated under reflux for 1 hr. Removal of the solvent, addition of H_2O, extraction with ether, and distillation under reduced pressure yielded valeranone (XI) as a colorless mobile oil, d_4^{25} 0.963, n_D^{25} 1.491, $[\alpha]_D$ −49.0° (c=10.4), *Anal.* Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.84; H, 11.86, IR (liquid) cm^{-1}: 1702 (carbonyl), NMR: singlet (3H) at 9.21 τ (CH_3-C<), doublet (6H) at 9.13 τ (J=7.1, $(CH_3)_2CH$-), singlet (3H) at 9.02 τ (CH_3-C<CO-). The identity was established by IR and NMR comparison and by preparation of the 2,4-dinitrophenylhydrazone which crystallized from EtOH in orange flat needles, m.p. 101.5~102°, *Anal.* Calcd. for $C_{21}H_{30}O_4N_4$: N, 13.92. Found: N, 13.87, undepressed on admixture with the authentic sample.

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Summary

Kanokonol, the sesquiterpenoid keto-alcohol isolated from Japanese valerians, has been shown to have stereostructure I (R=H) by means of spectral determinations and by conversion to the γ-lactone (IV) and to valeranone (XI).

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