was identified as 4-pyridone $H_2O$ (3.0 g., 26.5%), m.p. 64.5~65° (from $CHCl_3$), reported[15] 66~67°. No depression of melting point was observed on admixture with authentic sample.

**Reductive Benzylation of 2-Nitropyridine**——The reaction was conducted according to the *General Procedure.* 2-Benzylaminopyridine was obtained in 35.3% yield (Table I), m.p. 95~96° (from isopropyl alcohol), reported[5] m.p. 96~96.5° (corr.). On working up the aqueous layer in a similar manner as in preceding example, 0.8 g. (8.4%) of 2-pyridone was obtained, m.p. 107~107.5° (from benzene), reported[16] 104~106°. No depression of melting point was observed on admixture with authentic sample.

The authors wish to thank Miss H. Ohta of the Faculty of Pharmaceutical Sciences, Nagasaki University for microanalyses.

## Summary

Aromatic nitro compounds, when heated with benzyl alcohol and potassium hydroxide over 200°, underwent reductive benzylation to give aromatic benzylamines. Some side reactions were described.

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## 101. **Hiroshi Hikino, Yasuyoshi Takeshita, Yasuko Hikino, and Tsunematsu Takemoto**: Structure and Absolute Configuration of Fauronyl Acetate and Cryptofauronol.[*1]

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As part of investigations directed towards a study of the constituents of plants belonging to the valerianaceous family, we first carried out analysis of the essential oils of several cultivated Japanese valerians and found that these can be classified into two different series from the viewpoint of their chemical components.[1,2] Besides the cultivated valerians, there grows a wild valerian named "Kanoko-so" in the upper grasslands in the central and southern part of Japan. The taxonomical relationships of the original plants of those valerians have, however, not been clarified. Although no wild Japanese valerians seem to have been used medicinally, we examined the composition of the oil from a valerian indiginous to Mt. Ibuki with a view to investigating its relationship to the cultivated valerians from the standpoint of their chemical constituents and found that the composition was considerably different from those of the cultivated ones.[3] In this examination, we isolated two hitherto unknown sesquiterpenoids, fauronyl acetate and cryptofauronol, and, in a preliminary communication,[4] established their structure and absolute configuration as shown in formulae I

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[*1] This paper constitutes Part Ⅲ in the series on Sesquiterpenoids. Preceding paper, Part Ⅱ, H. Hikino, Y. Hikino, T. Takemoto: This Bulletin, **13**, 1417 (1965).
[*2] Kita-4-bancho, Sendai (ヒキノヒロシ, 竹下保義, 曳野靖子, 竹本常松).
[1] H. Hikino, Y. Hikino, H. Kato, Y. Takeshita, T. Takemoto: Yakugaku Zasshi, **83**, 219 (1963).
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and Ⅱ, respectively. The present paper describes the evidence in full detail.

Fauronyl acetate analyzed for $C_{17}H_{28}O_3$ and its molecular weight was confirmed by a mass spectrometric determination.

Our first endeavor was to establish the nature of the functional groups. The infrared spectrum shows the presence of a ketonic carbonyl in a six-membered or larger ring ($1695\,cm^{-1}$) and an acetoxyl group ($1733$ and $1234\,cm^{-1}$). The former function was demonstrated by preparing a crystalline semicarbazone (Ⅲ) and the latter by a nuclear magnetic resonance (NMR) singlet at $7.99\tau$. Further, the signal equivalent to one proton which must be assigned to the hydrogen on carbon attached to the acetoxyl group indicates the acetoxyl to be secondary. Three of the oxygen atoms are thereby accounted for.

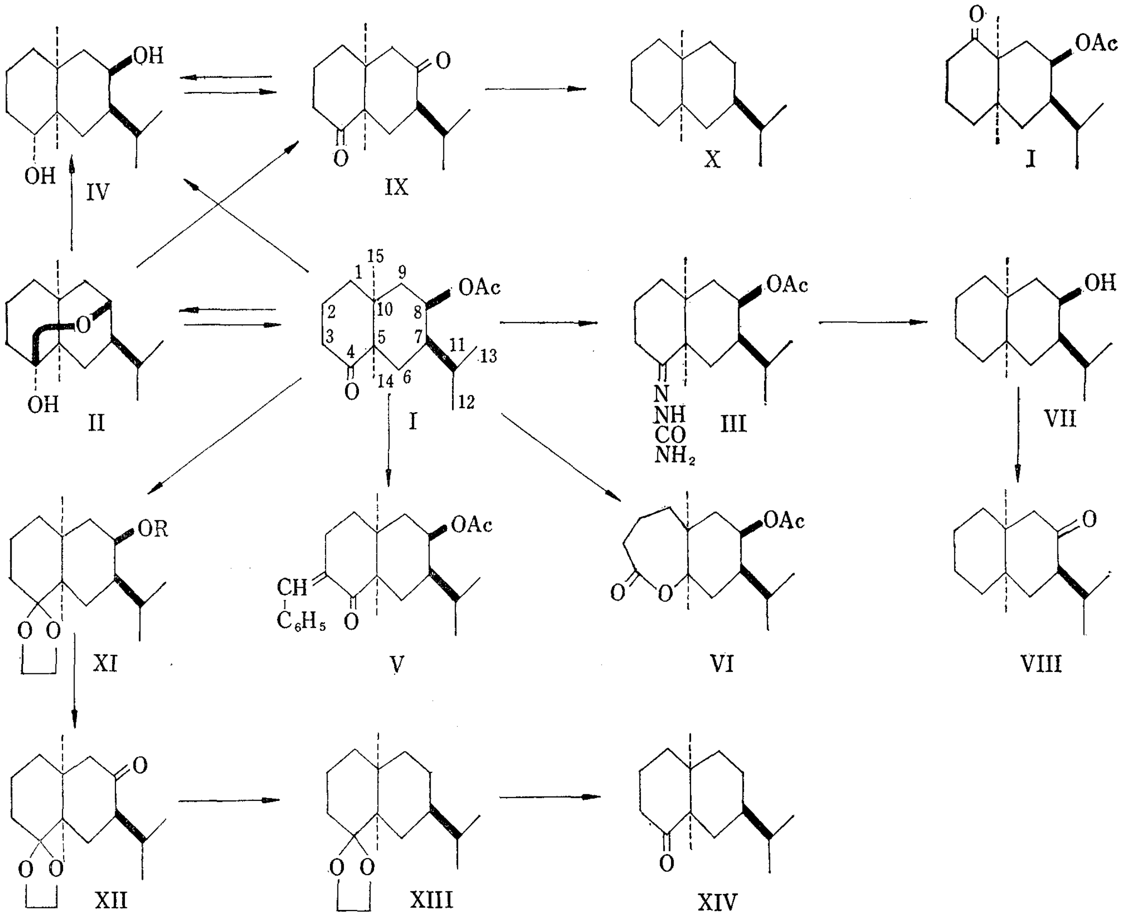

Chart 1.

Alkaline hydrolysis of fauronyl acetate gave the deacetyl-derivative, $C_{15}H_{26}O_2$, which was found to be identical with the natural cryptofauronol. On acetylation with refluxing acetic anhydride in the presence of sodium acetate, cryptofauronol was partly reconverted into fauronyl acetate. However, the infrared spectrum of cryptofauronol indicates the presence of a hydroxyl group but no carbonyl group. Lithium aluminum hydride reduction of both the substances afforded the same diol (Ⅳ). Therefore, the two interchangeable substances must be in the relation of a ketol acetate and a hemiketal of the free ketol.

The neighboring groups of the carbonyl in fauronyl acetate were then studied. The presence of a methylene group adjacent to the carbonyl followed from an infrared band at 1432 $cm^{-1}$ and the formation of the benzylidene derivative (V). The quarternary nature of the second carbon atom $\alpha$ to the carbonyl was established by perbenzoic acid oxidation of fauronyl acetate to give the lactone (Ⅵ), the NMR spectrum of which, however, showed no signal indicating the presence of a hydrogen on carbon attached to the lactonic oxygen.

For the investigation of the environment of the acetoxyl group in fauronyl acetate, the removal of the carbonyl group was required. For this purpose Huang-Minlon reduction of fauronyl acetate semicarbazone (Ⅲ) was carried out to yield an alcohol which was later deduced to be valeran-8$\beta$-ol (Ⅶ) from the half band width (7 c.p.s.) of the C-8 hydrogen signal in the NMR spectrum. On chromic acid oxidation, the alcohol (Ⅶ) afforded the ketone (Ⅷ). The position of the carbonyl group was confirmed as lying between a methylene and a methine group in the ketone (Ⅷ) by the facts described below. There is a band in the infrared at 1424 $cm^{-1}$ assigned to a methylene $\alpha$ to the carbonyl and an AB quadruplet equivalent to two protons in the NMR spectrum at 7.60 and 8.24 $\tau$ which indicates the methylene to be also adjacent to a fully substituted carbon atom. Base-catalyzed exchange of active hydrogens for deuterium converted the ketone (Ⅷ) into the trideuterio-derivative whose infrared spectrum no longer exhibited the band due to the deformation vibrations of the methylene $\alpha$ to the carbonyl but bands at 2212 and 2112 $cm^{-1}$ associated with the C-D stretching frequencies.

It is now required to establish the carbon skeleton which has been arrived at by the following way. Cryptofauronol or the diol (Ⅳ) was oxidized with chromic acid to give the diketone (Ⅸ). This has in its infrared a band at 1429 $cm^{-1}$ attributed to a methylene $\alpha$ to the carbonyl and in its NMR spectrum a 2H quadruplet in an AB type at 7.64 and 8.29$\tau$. Its deuterated derivative lacks the infrared band due to the active methylene and, in the NMR spectrum, has lost five protons, including the above AB quadruplet, as compared with the parent dione (Ⅸ). On Wolff-Kishner reduction, the diketone (Ⅸ) yielded a hydrocarbon which was identical in all respect with valerane (X). That no isomerization of the carbon skeleton occurred during the reaction from cryptofauronol to valerane (X) *via* the dione (Ⅸ) was established as follows: on reduction with lithium aluminum hydride the dione (Ⅸ) afforded the same diol (Ⅳ) which was obtained by reduction of fauronyl acetate and, in addition, the dione (Ⅸ) was not isomerized by alkali treatment.

After the carbon skeleton of fauronyl acetate has been established, arranging the partial structure described previously onto the valerane skeleton fixes the position of the acetoxyl group at C-8 which must further be in $\beta$-configuration from the fact that after hydrolysis it forms a hemiketal ring with the carbonyl group, and also the position of the carbonyl group at C-4 or C-1——that is, the possible formulation I or I′.

Of the remaining two positions of the carbonyl group, C-4 and C-1, both can be rationalized in terms of the hemiketal formation on hydrolysis, although structure I would require that the decalin ring interconverts (see below) and then the B (isopropyl bearing) ring be a boat form whilst in formula I′ it would take place immediately. Since the hydrogen at C-8 in the NMR spectrum of fauronyl acetate appears as an unresolved quadruplet with the coupling constant of approximate 3 c.p.s. showing the dihedral angles between the C-8 hydrogen and the three vicinal hydrogens to be all approximately 60°, *i.e.*, the C-8 hydrogen to be equatorial in the chair form or at a bow position in the boat conformation. Consequently, the C-7 isopropyl group is also in the equatorial orientation. However, severe steric compression between the 8$\beta$-acetoxyl group and the A (carbonyl bearing) ring excludes the alternative possibility that the B ring is a boat, therefore, the molecule must be in the all-chair conformation with the equatorial isopropyl group. In this conformation, the stereochemical environments of the carbonyl group in formula I and I′ correspond to those in 1-oxo-5$\beta$-steroids and 4-oxo-5$\beta$-methyl-steroids, respectively; both of which have been observed to give a negative Cotton effect (*e.g.*, $a=-136$ for methyl 1-oxo-5$\beta$-etianate⁵⁾ and $-75$ for 5-methylcoprostan-4-one,⁶⁾ respectively). A few more examples of the former are available in the sesquiterpenoids of this series ($a=-141$ for valeranone, $-149$ for kanokonol, and $-124$ for kanokonyl acetate⁷⁾). Experimentally, fauronyl acetate shows a negative Cotton effect ($a=-154$); the amplitude implies that it corresponds to the former.

Furthermore, the C-14 and C-15 methyl proton signals (9.02 and 9.20$\tau$, respectively) in the NMR spectrum of fauronyl acetate agree with those (9.02 and 9.21$\tau$, respectively) of valeranone.⁸⁾ In formulation I′, the C-5 methyl group is stereochemically situated in the same relation to the C-10 methyl group of 4-oxo-5$\beta$-steroids with respect to the carbonyl, while the C-10 methyl group to the C-10 methyl of 1-oxo-5$\alpha$-steroids. Carbonyl substitution effect on chemical shifts of the C-19 methyl protons has been estimated as $-0.20\sim-0.212$ p.p.m. in 4-oxo-5$\beta$-steroids and $-0.360\sim-0.384$ p.p.m. in 1-oxo-5$\alpha$-steroids.⁹⁾ These data lead to the conclusion that, on calculating from the chemical shifts of the C-14 and C-15 methyl proton signals of valerane (X) as standard, those of the C-14 and C-15 methyl protons of structure I′ can be predicted to be $\sim$8.94 and $\sim$8.78$\tau$, respectively; the latter is far different from the observed value (9.21$\tau$). This NMR evidence also suggests that in fauronyl acetate the carbonyl group is located at C-4. However, a conclusive decision could be made after the acetoxyl group had been removed from the C-8 position.

Fauronyl acetate was converted with ethylene glycol under acid catalysis to the ketal-acetate (XI; $R=COCH_3$), which on hydrolysis with alkali gave the ketal-alcohol (XI; $R=H$). Oxidation of the ketal-alcohol (XI; $R=H$) with chromium trioxide-pyridine complex afforded the ketal-ketone (XII) which without purification was reduced by the Wolff-Kishner method to give a ketal, identified as valeranone ketal (XIII). This when hydrolyzed with dilute hydrochloric acid, furnished the ketone whose properties were identical with those of valeranone (XIV).⁸⁾

The decision in favor of formula I for fauronyl acetate is indicated in this way; cryptofauronol is then represented by formula II.

Further, as discussed previously, fauronyl acetate has been shown to have the conformation in which the decalin ring has the all-chair form with the isopropyl group in the equatorial orientation, and cryptofauronol the rigid conformation in which the B ring is a boat form.

No definite chemical evidence has hitherto been presented for a *cis* ring junction of the valerane skeleton. However, on hydrolysis of fauronyl acetate (I) the formation of the hemiketal, cryptofauronol (II), now provides unambiguous chemical proof for it.

In the NMR spectra of the valerane derivatives having a hydroxyl or acetoxyl group at C-8, methyl protons of the C-7 isopropyl group are found to appear as two doublets by the influence of the C-8 oxygen function. This finding is in accordance with that observed in methyl protons of the isopropyl group of neomenthol and its acetate in which the oxygen functions and the isopropyl group are in the same stereochemical relationships.

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## Experimental*[3]

**Fauronyl Acetate**——$C_{17}H_{28}O_3$, mol. wt. 280 (mass spec.), m.p. 85~86°, $[\alpha]_D$ −77.6°(c=10.0), IR (KBr) $cm^{-1}$: 1733, 1234 (acetoxyl), 1695 (cyclohexanone), 1432 (methylene adjacent to carbonyl). NMR: singlet (3H) at 9.20 $\tau$ ($C\underline{H}_3$-C⩽), two doublets (3H, respectively) at 9.15 and 9.12 $\tau$ (J=6.2, $(C\underline{H}_3)_2CH$-), singlet (3H) at 9.02 $\tau$ ($C\underline{H}_3$-C⩽CO-), singlet (3H) at 7.99 $\tau$ ($C\underline{H}_3$-CO-O-), unresolved quadruplet (1H) at 4.90 $\tau$ (J=~3, $\underline{H}$-C⩽O-CO-$CH_3$).

The semicarbazone, prepared in the customary manner, crystallized from EtOH as colorless plates, m.p. 218.5~220°. *Anal.* Calcd. for $C_{18}H_{31}O_3N_3$: C, 64.06; H, 9.26; N, 12.45. Found: C, 64.35; H, 9.32; N, 12.56.

**Hydrolysis of Fauronyl Acetate**——A solution of fauronyl acetate (I) (1.0 g.) in 2*N* ethanolic KOH (20 ml.) was refluxed for 1 hr. Isolation of the product and crystallization from light petroleum gave cryptofauronol (II) as colorless prisms, m.p. 90~91°, $[\alpha]_D$ −7.4° (c=7.0). *Anal.* Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.47; H, 10.84. IR (KBr) $cm^{-1}$: 3390 (hydroxyl). NMR: singlet (3H) at 9.15 $\tau$ ($C\underline{H}_3$-C⩽), two doublets (3H, respectively) at 9.11 and 9.10 $\tau$ (J=~6, $(C\underline{H}_3)_2CH$-), singlet (3H) at 9.06 $\tau$ ($C\underline{H}_3$-C⩽CO-), singlet (1H) at 7.67 $\tau$ (O$\underline{H}$), unresolved doublet (1H) at 6.08 $\tau$ (J=~4, $\underline{H}$-C⩽O-). This was identified as a sample of natural source in the usual criteria.

**Acetylation of Cryptofauronol**——Cryptofauronol (1.1 g.) was acetylated ($Ac_2O$-AcONa) by refluxing for 4 hr. Upon isolation, the product (1.3 g.) was filtered through alumina (40 g.).

Benzene eluted crystalline fractions (0.7 g.) crystallized from light petroleum to give fauronyl acetate (I) as colorless prisms, m.p. 85~86°, showing the identical IR spectrum and no m.p. depression on admixture with an authentic sample.

Succesive elution with benzene gave the other crystalline fractions (0.5 g.) crystallized from light petroleum to yield the recovered material, cryptofauronol (II), as colorless prisms, m.p. 89.5~91°, $[\alpha]_D$ −6.6°(c=2.4), which was undepressed when mixed with an authentic specimen. IR spectra of both samples were identical.

**Reduction of Fauronyl Acetate with Lithium Aluminum Hydride**——Fauronyl acetate (0.19 g.) and $LiAlH_4$ (0.10 g.) in ether (10 ml.) were stirred at room temperature for 2 hr. After isolation, the product (0.17 g.) was crystallized from light petroleum to give valerane-4$\alpha$,8$\beta$-diol (IV) as colorless needles, m.p. 112~113°, $[\alpha]_D$ +33.0°(c=4.6). *Anal.* Calcd. for $C_{15}H_{28}O_2\cdot\frac{1}{2}H_2O$: C, 72.24; H, 11.72. Found: C, 71.90; H, 11.29. IR (KBr) $cm^{-1}$: 3390 (hydroxyl). This semihydrate, when dried at 50° *in vacuo* (pressure 0.3 mm. Hg) for 3 days, lost 3.61% of its weight (theoretically 3.72%) to give the anhydrous diol as a colorless oil. *Anal.* Calcd. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.72; H, 11.36. NMR: two doublets (3H, respectively) at 9.10 and 9.08 $\tau$ (J=~6, $(C\underline{H}_3)_2CH$-), singlet (6H) at 9.02 $\tau$ ($C\underline{H}_3$-C⩽), unresolved band (band width at half height: 5 c.p.s., 1H) at 6.68 $\tau$ ($\underline{H}$-C⩽OH), unresolved band (band width at half height: 6 c.p.s., 1H) at 6.00 $\tau$ ($\underline{H}$-C⩽OH).

**Reduction of Cryptofauronol with Lithium Aluminum Hydride**——Cryptofauronol (140 mg.) in ether (15 ml.) was stirred with excess $LiAlH_4$ for 3.5 hr. at room temperature. Working up in the customary manner and crystallization of the product (140 mg.) from light petroleum gave the diol (IV) as colorless needles, m.p. 109~110°. *Anal.* Calcd. for $C_{15}H_{28}O_2\cdot\frac{1}{2}H_2O$: C, 72.24; H, 11.72. Found: C, 72.39; H, 11.57. The identity was confirmed by the usual criteria.

**Reaction of Fauronyl Acetate with Benzaldehyde**——Benzaldehyde (0.15 g.; freshly distilled) was added to fauronyl acetate (0.16 g.) in EtOH (2 ml.) and KOH solution (0.5 ml.; 30%), let stand at room temperature for 6 hr. and refluxed for a further 0.5 hr. The product (0.22 g.) was chromatographed on neutral alumina (20 g.). Elution with benzene and crystallization from light petroleum afforded the benzylidene derivative (V) as colorless needles, m.p. 139~140.5°, $[\alpha]_D$ −225.1°(c=3.9). *Anal.* Calcd. for $C_{24}H_{32}O_3$: C, 78.22; H, 8.75. Found: C, 78.28; H, 8.75. UV $\lambda_{max}^{EtOH}$ m$\mu$ (log $\varepsilon$): 290.5 (4.47). IR (KBr) $cm^{-1}$: 1736, 1236 (acetoxyl), 1672 (unsaturated carbonyl), 1597, 1151, 697 (phenyl).

**Baeyer-Villiger Oxidation of Fauronyl Acetate**——Fauronyl acetate (100 mg.) and perbenzoic acid (350 mg.) in $CHCl_3$ (10 ml.) was set aside at 25° for 7 days. The product (92 mg.) was chromatographed on a column of silica gel (3 g.). Elution with light petroleum and crystallization from light petroleum gave the lactone (VI) as colorless cubes, m.p. 98.5~100°, $[\alpha]_D$ −58.1° (c=2.3). *Anal.* Calcd. for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.75; H, 9.27. IR (KBr) $cm^{-1}$: 1733 ($\varepsilon$-lactone), 1724, 1242 (acetoxyl). NMR: two doublets (3H, respectively) at 9.15 and 9.04 $\tau$ (J=~6, $(C\underline{H}_3)_2CH$-), singlet (3H) at 8.98 $\tau$ ($C\underline{H}_3$-C⩽), singlet (3H) at 8.64 $\tau$ ($C\underline{H}_3$-C⩽O-), singlet (3H) at 8.03 $\tau$ ($C\underline{H}_3$-CO-O-), unresolved band (1H) at 5.00 $\tau$ ($\underline{H}$-C⩽O-CO-$CH_3$).

**Wolff-Kishner Reduction of Fauronyl Acetate Semicarbazone**——Fauronyl acetate semicarbazone (III) (400 mg.) in triethylene glycol (9 ml.) was heated with 80% $NH_2NH_2\cdot H_2O$ (1.5 ml.) and KOH (0.3 g.) at 195~

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*[3] Melting points are uncorrected. Specific rotations were measured in $CHCl_3$ solution. NMR spectra were determined at 60 Mc.p.s. in $CCl_4$ solution *vs.* $(CH_3)_4Si$ as internal reference. Chemical shifts are given in $\tau$-values and coupling constants (J) in c.p.s.

200° for 7 hr. After isolation, the product (150 mg.) was placed on alumina column (10 g.) and eluted with light petroleum-benzene (1:1) to yield a crystalline substance (114 mg.) which on crystallization from dil. MeOH afforded valeran-8$\beta$-ol (VII) as colorless prisms, m.p. 64.5~65°, $[\alpha]_D$ +61.3°(c=8.3). *Anal.* Calcd. for $C_{15}H_{28}O$ : C, 80.29; H, 12.58. Found : C, 79.93; H, 12.22. IR (KBr) $cm^{-1}$ : 3497, 3401 (hydroxyl). NMR : singlet (3H) at 9.20 $\tau$ ($C\underline{H}_3$-$C\leqslant$), singlet (3H) at 9.17 $\tau$ ($C\underline{H}_3$-$C\leqslant$), two doublets (3H, respectively) at 9.10 and 9.08 $\tau$ (J=~6, $(C\underline{H}_3)_2CH$-), unresolved band (band width at half height : 7 c.p.s., 1H) at 6.03 $\tau$ ($\underline{H}$-$C\leqslant OH$).

**Oxidation of Valeran-8$\beta$-ol with Chromic Acid**——The alcohol (VII) (150 mg.) in ether (10 ml.) was stirred with $Na_2Cr_2O_7 \cdot 2H_2O$ (0.20 g.) in $H_2SO_4$ (0.23 g.) and $H_2O$ (3 ml.) at room temperature for 6 hr. The product (140 mg.) from ether extraction was chromatographed on silica gel (1.5 g.). Elution with light petroleum and distillation under diminished pressure gave valeran-8-one (VIII) as colorless oil. $n_D^{25}$ 1.487, $[\alpha]_D$ +59.9° (c=13.0), mol. wt. 222 (mass spec.). *Anal.* Calcd. for $C_{15}H_{26}O$ : C, 81.02; H, 11.79. Found : C, 80.95; H, 11.53. IR (liquid) $cm^{-1}$ : 1715 (cyclohexanone), 1424 (methylene adjacent to carbonyl). NMR : two doublets (3H, respectively) at 9.14 and 9.09 $\tau$ (J=6.0, $(C\underline{H}_3)_2CH$-), singlet (3H) at 9.02 $\tau$ ($C\underline{H}_3$-$C\leqslant$), singlet (3H) at 8.87 $\tau$ ($C\underline{H}_3$-$C\leqslant$), quadruplet (2H) in an AB system at 8.24 and 7.60 $\tau$ (J=14.0, $\geqslant C$-$C\underline{H}_2$-CO-).

**Base-catalyzed Deuteration of Valeran-8-one**——Valeran-8-one (VIII) (15 mg.) in $D_2O$ (0.5 ml.) and dioxane (1.5 ml.) was refluxed for 10 min. with NaOD (20 mg.) and the solvent was removed *in vacuo.* This process was repeated four times. Distillation of the product yielded the trideuteriovaleran-8-one as a colorless oil, mol. wt. 225 (mass spec.). IR (liquid) $cm^{-1}$ : 2212, 2123 (C-D), 1715 (cyclohexanone).

**Oxidation of Cryptofauronol with Chromic Acid**——To cryptofauronol (230 mg.) in ether (12 ml.) was added $Na_2Cr_2O_7 \cdot 2H_2O$ (263 mg.) in conc. $H_2SO_4$ (350 mg.) and $H_2O$ (4 ml.) and the mixture was stirred 5 hr. at room temperature. Upon isolation with ether, the product (229 mg.) was chromatographed over alumina (20 g.).

Elution with benzene and distillation under reduced pressure afforded valerane-4,8-dione (IX) as a colorless oil. $n_D^{25}$ 1.496, $[\alpha]_D$ −30.6°(c=7.4). *Anal.* Calcd. for $C_{15}H_{24}O_2$ : C, 76.22; H, 10.24. Found: C, 76.22; H, 9.90. IR (liquid) $cm^{-1}$ : 1709 (cyclohexanone), 1429 (methylene adjacent to carbonyl). NMR: two doublets (3H, respectively) at 9.12 and 9.05 $\tau$ (J=6.6, $(C\underline{H}_3)_2CH$-), singlet (3H) at 9.07 $\tau$ ($C\underline{H}_3$-$C\leqslant$), singlet (3H) at 8.85 $\tau$ ($C\underline{H}_3$-$C\leqslant CO$-), quadruplet (2H) in an AB system at 8.29 and 7.64 $\tau$ (J=13.2, $\geqslant C$-$C\underline{H}_2$-CO-).

Elution with MeOH gave the recovered cryptofauronol.

**Oxidation of Valerane-4$\alpha$,8$\beta$-diol with Chromic Acid**——To the diol (IV) (50 mg.) in ether (10 ml.) was added $Na_2Cr_2O_7 \cdot 2H_2O$ (200 mg.) in $H_2SO_4$ (200 mg.) and $H_2O$ (3 ml.) and the mixture was stirred at room temperature for 2 hr. The product (48 mg.) isolated in the usual manner was chromatographed over alumina (6 g.). A mixture of light petroleum and benzene (1:1) eluted an oil (27 mg.) which on distillation under reduced pressure yielded the dione (IX). Identification was carried out in the usual criteria.

**Base-catalyzed Deuteration of Valerane-4,8-dione**——Deuterium exchange of valerane-4,8-dione (IX) (95 mg.) was performed by the similar procedure described in base-catalyzed deuteration of valeran-8-one (VIII). The product (67 mg.) was distilled under diminished pressure to give the pentadeuteriovalerane-4,8-dione. IR (liquid) $cm^{-1}$ : 2212 (C-D), 1709 (cyclohexanone). NMR : two doublets (3H, respectively) at 9.15 and 9.08 $\tau$ (J=5.9, $(C\underline{H}_3)_2CH$-), singlet (3H) at 9.04 $\tau$ ($C\underline{H}_3$-$C\leqslant$), singlet (3H) at 8.87 $\tau$ ($C\underline{H}_3$-$C\leqslant CO$-).

**Wolff-Kishner Reduction of Valerane-4,8-dione**——The dione (IX) (150 mg.) in EtOH (1 ml.) was refluxed for 1 hr. with 80% $NH_2NH_2 \cdot H_2O$ (0.2 ml.). After the addition of KOH (0.3 g.), and triethyleneglycol (1 ml.), $NH_2NH_2 \cdot H_2O$ and EtOH were then removed by distillation and the mixture was kept at 190~195° for 4 hr. The product (111 mg.) was isolated with ether and filtered through alumina (3 g.). Elution with light petroleum and distillation under reduced pressure afforded valerane (X) as a colorless mobile oil. $n_D^{25}$ 1.481, $[\alpha]_D$ +86.8° (c=10.0). *Anal.* Calcd. for $C_{15}H_{28}$ : C, 86.46; H, 13.54. Found : C, 86.78; H, 13.42. NMR : singlet (6H) at 9.15 $\tau$ ($C\underline{H}_3$-$C\leqslant$), doublet (6H) at 9.13 $\tau$ (J=4.7, $(C\underline{H}_3)_2CH$-). Identification was performed by behavior upon VPC (Carbowax 6000) and IR and NMR spectra.

**Reduction of Valerane-4,8-dione with Lithium Aluminum Hydride**——The dione (IX) (48 mg.) and excess $LiAlH_4$ in ether (20 ml.) was stirred 5 hr. at room temperature. The reduction product (49 mg.) was crystallized from light petroleum to give the diol (IV) as colorless needles, m.p. 112~113°, $[\alpha]_D$ +32.1° (c=4.9). *Anal.* Calcd. for $C_{15}H_{28}O_2 \cdot \frac{1}{2}H_2O$ : C, 72.24; H, 11.72. Found : C, 72.42; H, 11.59, which was shown by IR and NMR spectra and mixed melting point to be identical with the diol (IV).

**Treatment of Valerane-4,8-dione with Alkali**——a) The dione (IX) (50 mg.) in *N* ethanolic KOH solution (3 ml.) was left standing at room temperature for 24 hr. Isolation of the product (44 mg.) followed by distillation gave the recovered dione (IX). $n_D^{25}$ 1.490, $[\alpha]_D$ −25.6°(c=2.5), which was shown by VPC (GE silicone SE 30), TLC (silica gel, benzene-AcOEt=10:3), IR and NMR spectra to be identical with the starting dione (IX).

b) The dione (IX) (79 mg.) was refluxed 3 hr. in *N* ethanolic KOH solution (5 ml.) under $N_2$. Distillation of the product (61 mg.) afforded the dione (IX). $n_D^{25}$ 1.495, $[\alpha]_D$ −25.1°(c=6.2), which was identified by VPC, TLC, IR and NMR spectra.

**Ketalization of Fauronyl Acetate**——Fauronyl acetate (100 mg.), ethylene glycol (5 ml.) and *p*-toluenesulfonic acid (20 mg.) in benzene (25 ml.) were refluxed for 18 hr. during which period the separated $H_2O$ was taken off. The product (92 mg.) was crystallized from light petroleum gave the ethylene ketal (XI; $R=COCH_3$) as colorless plates, m.p. 114~115°, $[\alpha]_D$ −27.7°(c=7.7). *Anal.* Calcd. for $C_{19}H_{32}O_4$ : C, 70.33; H, 9.94. Found : C, 70.04; H, 9.67. IR (KBr) $cm^{-1}$ : 1733, 1239 (acetoxyl), 1195, 1075 (ketal).

**Hydrolysis of Fauronyl Acetate Ethylene Ketal**——Fauronyl acetate ethylene ketal (XI; $R=COCH_3$)

(362 mg.) was refluxed 4 hr. with *N* ethanolic KOH solution (5 ml.). Isolation of the product (322 mg.) by ether extraction and crystallization from light petroleum yielded fauronol ethylene ketal (XI; R=H) as colorless needles, m.p. 85.5~86.5°, $[\alpha]_D$ +31.3°(c=5.6). *Anal.* Calcd. for $C_{17}H_{30}O_3$ : C, 72.30; H, 10.71. Found : C, 71.94; H, 10.68. IR (KBr) $cm^{-1}$ : 3401 (hydroxyl), 1195, 1082 (ketal).

**Oxidation of Fauronol Ethylene Ketal with Chromium Trioxide-Pyridine Complex**——Fauronol ethylene ketal (XI; R=H) (160 mg.) in pyridine (4 ml.) was added to $CrO_3$ (500 mg.) in pyridine (4 ml.) and let stand at room temperature for 7 hr. The solvent was evaporated *in vacuo* and the residue extracted with ether. The ether solution was washed, dried, and evaporated yielding the crude ketal-ketone (XII) (138 mg.) as a pale yellow liquid, IR (liquid) $cm^{-1}$ : 1712 (cyclohexanone), 1195, 1080 (ketal), which appeared as mainly one spot upon TLC (silica gel, benzene-AcOEt=10:3).

**Wolff-Kishner Reduction of the Ketal-ketone**——The crude ketal-ketone (XII) (135 mg.) and 80% $NH_2NH_2 \cdot H_2O$ (0.5 ml.) in EtOH (3 ml.) were refluxed for 4 hr. Triethylene glycol (3 ml.) was added and the mixture was heated at 170° for 30 min. to remove EtOH, $H_2O$, and $NH_2NH_2$ by distillation. Then KOH was added and the mixture was heated at 195±5° for 2 hr. Upon isolation, the product (112 mg.) was filtered through alumina (10 g.). Elution with light petroleum and distillation under reduced pressure gave deoxyfauronol ethylene ketal (XIII) as a colorless oil, $n_D^{25}$ 1.489, $[\alpha]_D$ +12.7°(c=4.7). *Anal.* Calcd. for $C_{17}H_{30}O_2$ : C, 76.64; H, 11.35. Found : C, 76.36; H, 11.12. IR (liquid) $cm^{-1}$ : 1198, 1078 (ketal), which was identified as valeranone ethylene ketal by comparison of behaviors on VPC (GE silicone SE 30) and TLC (silica gel, benzene-AcOEt=10:3) and of the IR spectra.

**Hydrolysis of Deoxyfauronol Ethylene Ketal**——Deoxyfauronol ethylene ketal (XIII) (38 mg.) was refluxed 1 hr. with aqueous ethanolic HCl solution, prepared from conc. HCl (0.5 ml.), $H_2O$ (0.5 ml.) and EtOH (3.5 ml.). Upon isolation, the product (30 mg.) was chromatographed on alumina (3 g.). After percolation with light petroleum, light petroleum-benzene (1:1) eluted an oil distilled under reduced pressure to give valeranone (XIV) as a colorless oil, $n_D^{25}$ 1.490, $[\alpha]_D$ −40.9°(c=2.6). *Anal.* Calcd. for $C_{15}H_{26}O$ : C, 81.02; H, 11.79. Found : C, 81.32; H, 11.67. IR (liquid) $cm^{-1}$ : 1702 (cyclohexanone). NMR : singlet (3H) at 9.21 τ ($C\underline{H}_3$-C⋖), doublet (6H) at 9.13 τ (J=7.1, $(C\underline{H}_3)_3CH$-), singlet (3H) at 9.02 τ ($C\underline{H}_3$-C⋖CO-). The identity was confirmed by identical behaviors upon VPC (GE silicone SE 30) and TLC (silica gel, benzene-AcOEt=10:3) and by identical IR and NMR spectra.

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## Summary

The structure and absolute stereochemistry of fauronyl acetate and cryptofauronol have been elucidated as formulae I and II, respectively, by the following series of reactions coupled with spectral determinations. Fauronyl acetate (I) and cryptofauronol (II) were interconverted by hydrolysis and acetylation. Fauronyl acetate was transformed to the ketone (VIII), in which the environment of the carbonyl group was established, and to valeranone whose absolute stereostructure (XIV) is known.

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