indole derivatives (Va–Vd). With a little excess of lithium aluminum hydride IVd gave a indoline derivative (VIII) together with the cyclized base (Vd) though the latter of which could not be cleaved by lithium aluminum hydride even under more strenuous condition.

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Yoshikazu Kondo,[*1] **Tsuneo Ikenoue,**[*2] **and Tsunematsu Takemoto**[*1] : Structure of Xanthoperol.

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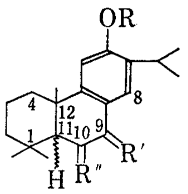
Xanthoperol is a phenolic diterpene which was isolated from *Juniperum communis* L. by Bredenberg, *et al.*1)

Recently, Bredenberg and Shoolery2) measured the nuclear magnetic resonance spectrum (NMR) of xanthoperol and recognized the fact that V was more compromising than the previously suggested structure.3) Further on A/B ring juncture, possibility of *cis* was noted. However, since they employed the external referene and did not correct the effect of diamagnetic bulk susceptibility, methyl signal was appeared in the low field.



I : $R=H;\ R'=R''=H_2,\ 11\alpha$
II : $R=Ac;\ R'=R''=H_2,\ 11\alpha$
III : $R=H;\ R'=O;\ R''=H_2,\ 11\alpha$
IV : $R=Ac;\ R'=O;\ R''=H_2,\ 11\alpha$
V : $R=H;\ R'=R''=O,\ 11\beta$
VI : $R=Ac;\ R'=R''=O,\ 11\beta$

Ferruginol (I), sugiol (III) and xanthoperol which were isolated from the wood resin of *Cryptomeria japonica* D. Don4) were kindly supplied by professor T. Kondo and they were converted to ferruginol acetate (II), sugiol acetate (IV) and xanthoperol acetate (VI) respectively. By the comparison of their NMR, authors observed the significant difference in methyl signal of xanthoperol acetate from those of two others.

The NMR of II, IV and VI measured in chloroform solution are shown in Figs. 1, 2 and 3.

In Fig. 1, the signal appeared in 9.04 (τ') corresponds to six protons and was assigned to *gem*-methyl (e) and angular methyl groups; signals 8.83 (τ') and 8.70 (τ'), in the observation of slow seep, both split into doublet so they must belong to isopropyl group; and signal 8.78 (τ') will be assigned to *gem*-methyl group (a).

In Fig. 2, *gem*-methyl (e) and angular methyl groups are appeared separately in 9.01 (τ') and 9.07 (τ'). And C_8 in ring protons shifts to 2.04 (τ') by the effect of paramagnetic shielding of carbonyl group.

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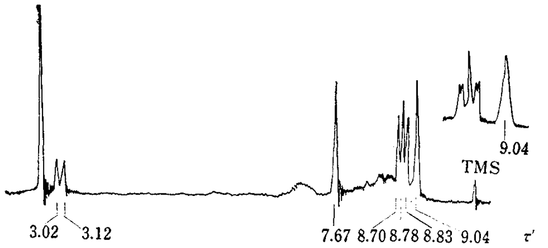

Fig. 1. Nuclear Magnetic Resonance Spectrum of Ferruginol Acetate (in $CHCl_3$)

Fig. 2. Nuclear Magnetic Resonance Spectrum of Sugiol Acetate (in $CHCl_3$)

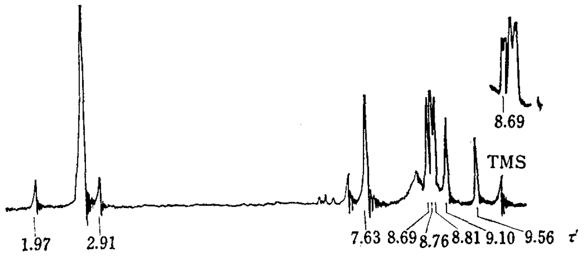

Fig. 3. Nuclear Magnetic Resonance Spectrum of Xanthoperol Acetate (in $CHCl_3$)

In the NMR of VI (Fig. 3), one of the methyl groups shifts into high field, 9.56 (τ'). In VI, B and C rings are maintained in coplanar since there are two carbonyl groups introduced into B ring. Now if A/B ring juncture is posturated to be in *trans* junction, angular methyl and *gem*-methyl groups (a) will be in a relation of 1,3-diaxial, and both of methyl groups are expected to shift into low field, but actually, only one of the methyl groups shifts into high field approximately 0.5 p.p.m. The anisotropy of carbonyl group and benzene ring are considered to be the most appropriate reason for this fact. From this reason the possibility of *trans* junction is contradictory. If A/B ring juncture is *cis*, among *gem*-methyl groups, axial methyl group make entry in inside of the diamagnetic shielding of two carbonyl groups and benzene ring and, in turn, it can be expected to shift into high field. This consistent exactly with the findings of our experiments. Moreover, in the observation of slow seep, methyl groups with exception of isopropyl group indicate perfect singlet. From the results above obtained the actual conformation of xanthoperol was concluded to be 6-hydroxy-7-isopropyl-9,10-dioxo-1*α*,1*β*,4a*β*-trimetyl-10a*β*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (V, 11*β*).

Experimental

Materials——Since I, III and V did not have a sufficient solubility in organic solvents except in pyridine, II, IV and VI which were acetylated with Ac_2O and pyridine were employed for the measurement of spectra in this study. The physical constants of these compounds are listed in Table I.

Table I.

	m.p.[a] (°C)	[α]D	Ref.
Ferruginol (I)	57～59	+50.0	
Ferruginol acetate (II)	81～82	+53.04	4
Sugiol (III)	283～290	+30.6	4
Sugiol acetate (IV)	162～163	+26.7	
Xanthoperol (V)	246 (decomp.)[b]	+142.6	1, 4
Xanthoperol acetate	156～157	—	

a) All melting points are uncorrected.
b) Decomposes between 255～270°.[1]

Procedures——These acetates were dissolved in $CHCl_3$ at 0.5 molar concentration and degased in high vacuum apparatus ($10^{-5.3}\sim10^{-4.7}$ mm. Hg). All spectra were obtained as 60 Mc. p. s. with a Varian V-4311 NMR spectrometer. Tetramethylsilane was used at internal standard. Calibrations of the spectra were carried out by the standard separation between benzene-cyclohexane mixture as 5.75 p.p.m. Values are expressed in 10 δ p.p.m. $=\tau'$ (TMS $=0$ p.p.m.).

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