Next, the absolute structure of schizandrin (V)[2,6] was determined by the measurements of NOE(in $CDCl_3$) and circular dichroism (CD) spectrum. As shown in Fig. 1, the results of NOE indicated that schizandrin has the same conformational structure as IX. On the other hand, the CD spectrum of V(in MeOH) showed two positive Cotton effects at 250 ($[\theta]$ +95000) and 235 nm ($[\theta]$ +75000), and a negative at 214 nm ($[\theta]$ −100000), indicating that V possesses *R*-biphenyl configuration.[1b,c]

On the basis of the above observations, the absolute structures of angeloylgomisin H, tigloylgomisin H, benzoylgomisin H and schizandrin are expressed by the formulae I, II, III and V, respectively.

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6) Quite recently, Y.P. Chen, *et al.* suggested that schizandrin has *trans*-dimethyl groups at C_7 and C_8(Yuh-Pan Chen, Rolan Liu, Hon-Yen Hsu, S. Yamamura, Y. Shizuri and Y. Hirata, *Bull. Chem. Soc. Japan*, **50**, 1824 (1977)). However, we believe that our assumption should be correct considering the results of spectral analyses as described above together with the results of C. Yan-Yang, *et al.* supporting that schizandrin has *cis*-dimethyl groups (Chen Yan-Yang, Shu Zeng-Bao and Li Lianf-Nianf, *Scientia Scinica* (Peking), **19**, 276 (1976)).

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Structure of Gilvanol, a New Triterpene isolated from *Quercus gilva* Blume

A new triterpene named Gilvanol (Ia), $C_{30}H_{50}O_4$, mp 212—215°, which have been elucidated to be hopan-3β-ol-17(21)-ozonide by chemical evidence and X-ray analysis, was isolated from *Quercus gilva* Blume.

Keywords——triterpene; hopane; gilvanol; ozonide; X-ray analysis; *Quercus gilva* Blume.

Previously, we reported about nine triterpenes isolated from *Quercus gilva* Blume.[1,2] One of them named as D-20 was not yet elucidated structurally. Now, we wish to report the structure of D-20 named as Gilvanol.

Gilvanol (Ia), $C_{30}H_{50}O_4$, mp 212—215°, possessed one hydroxy function (3410 cm^{-1}) by its infrared spectrum (IR), six tertiary methyls, two secondary methyls by its proton magnetic resonance (PMR) using $Eu(dpm)_3$ as a shift reagent, and showed the signal at δ 3.30 assignable to 3α-H. By mass spectrum of (Ia), the fragment ion peaks were observed at m/e 474 (M^+), 456 (M^+-H_2O), 207, 189 and 135 which had been characterized as the hopane skeleton.[3] On the other hand, the nature of three other oxygen atoms, was presumed to be an ozonide functional group, since no proton neighbouring to those oxygen atoms was observed by PMR and characteristic signals appeared at δ 112.4 ppm and 111.8 ppm on ^{13}C-nuclear magnetic resonance (^{13}C–NMR) spectrum.

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1) Y. Kamano, Y. Tachi, T. Otake, J. Sawada, and I. Tanaka *Yakugaku Zasshi*, **96**, 1202 (1976).
2) Y. Tachi, Y. Kamano, J. Sawada, I. Tanaka, and H. Itokawa, *Yakugaku ZAsshi*, **96**, 1213 (1976).
3) G.R. Waller, "Biochemical Applications of Mass Spectrometry," Wiley-Interscience, 1972.

Gilvanol was converted to acetate (Ib) ($C_{32}H_{52}O_5$, mp 215—216°), on Ac_2O–pyridine, to *p*-bromobenzoate (Ic) ($C_{37}H_{53}BrO_5$, mp 212—213°) on *p*-bromobenzoyl chloride, and to ketone (Id) ($C_{30}H_{48}O_4$, mp 197—200°), on CrO_3–pyridine. These derivatives showed the presence of 3β-OH in (Ia). In addition, Ia was treated with $LiAlH_4$ to give two main compounds (IIa, b) which were isolated by SiO_2 column chromatography. IIa ($C_{30}H_{54}O_3$, mp 162—165°) and IIb ($C_{30}H_{54}O_3$, mp 211—213°) possessed three hydroxy functions (3390 cm^{-1}; IR) which afforded triacetate respectively. Further, Ia was treated with dil. HCl or Zn–AcOH to give dione (III) ($C_{30}H_{50}O_3$, mp 70—72° (powder)), which on $NaBH_4$ reduction, gave smoothly IIa and IIb (Chart 1). In order to prove the assumption, the X-ray analysis of Ic has been undertaken as described below.

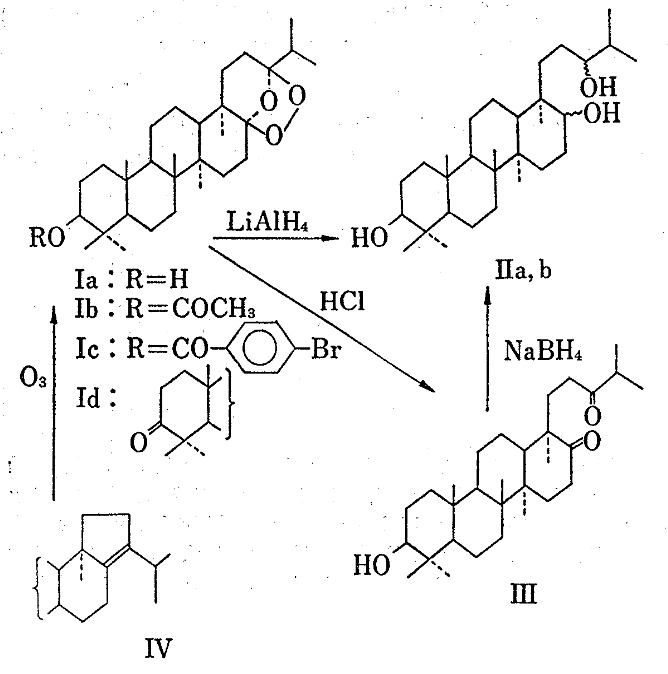


Chart 1

The crystals grown from a *n*-hexane solution were colorless transparent plates with well developed 100 faces.

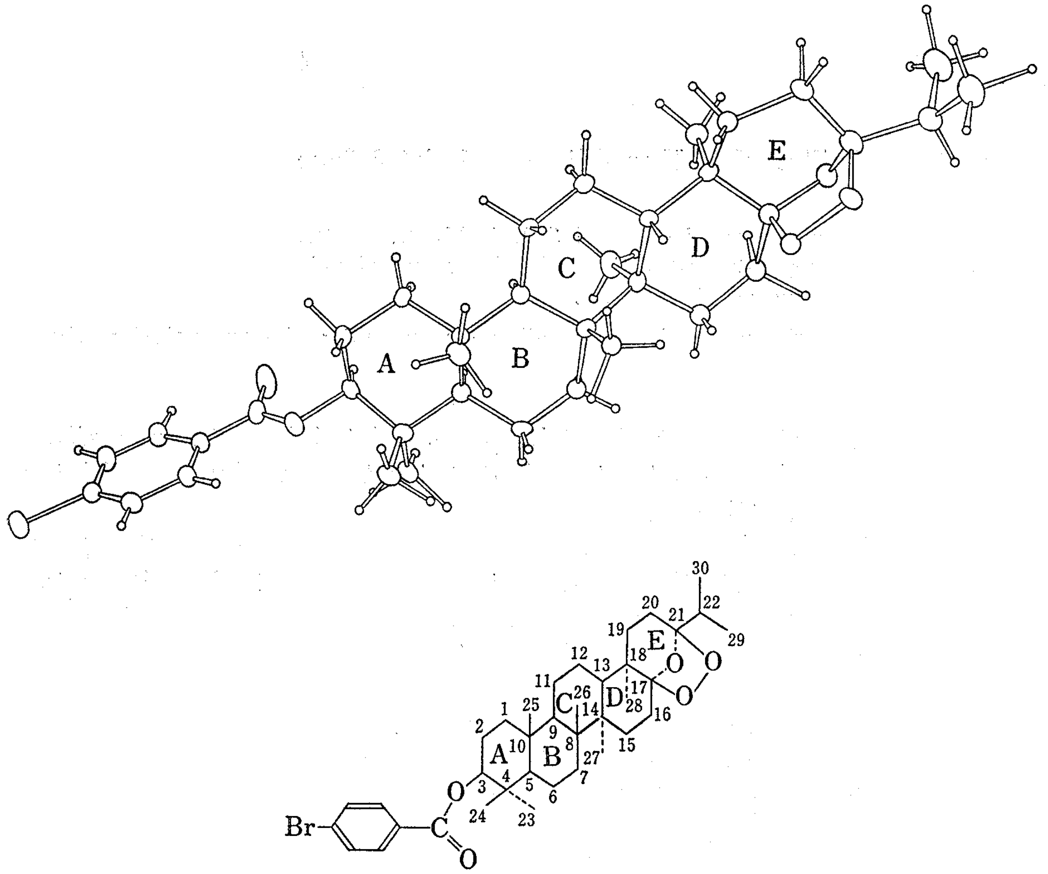


Fig. 1. The Molecular Structure of Gilvanol *p*-Bromobenzoate

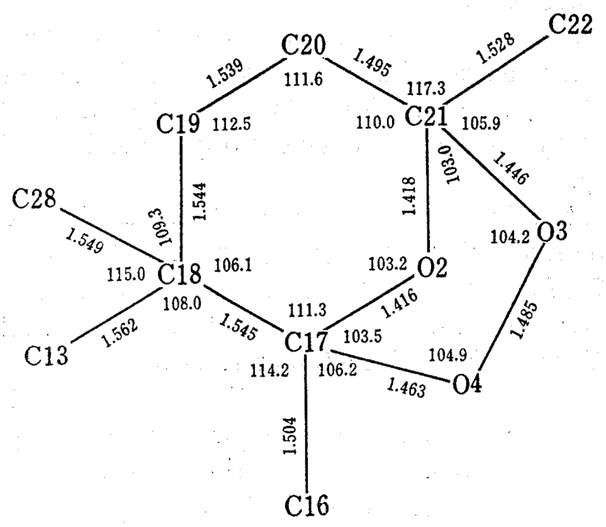
The perspective drawing which shows the stereo-structure in absolute configuration, was plotted by the ORTEP program (Johnson[4]). The atoms are shown by the ellipsoid covering the 20% probability region of finding the centre of the atom in it.

Diffraction data were obtained for the crystal with approximate dimensions 0.5×0.13×0.02 mm on a Philips fourcircle X-ray diffractometer using graphite monochromated Cu K_α radiation. Crystal data are shown as follows, Gilvanol *p*-bromobenzoate, $C_{37}H_{53}BrO_5$, M.W.=656, mp 212—213°. Monoclinic, $a=31.91(2)$, $b=6.562(5)$, $c=16.50(1)$ Å, $\beta=104.9(1)°$, Space group C2, $z=2$.

The structure was solved by the heavy atom method. Successive use of Fourier and difference Fourier syntheses, coupled with block-diagonal least-squares calculations established the structure as shown in Fig. 1. All the 53 hydrogen atoms were located on the difference electron density map and their atomic parameters were refined by the least-squares calculations. The oxygen atoms were distinguished from the carbon atom on the difference electron density map. The anomalous dispersion effect of the bromine atom was taken into account assuming the absolute configuration determined by comparison of intensity ratios between the 794 Friedel pairs. The final R value was 0.05 for 2838 observed reflexions.

The chemical structure of gilvanol has now been established as shown in Fig. 1 including absolute configuration. Gilvanol is the first compound isolated from natural sources having ozonide in its molecule. And it was synthesized by the ozonolysis of hop-17(21)en-3β-ol(IV).

The bond lengths, angles and conformations are in good overall agreement with those reported for triterpenes. The values found in E ring involving the –O–O– bridge are depicted in Fig. 2.



02-C21-C22	109.2°
03-C21-C20	110.4
04-C17-C18	109.8
02-C17-C16	111.2
C17-C18-C28	109.1
C13-C18-C19	109.0

Fig. 2. Bond Lengths and Bond Angles at the Ring E

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