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THE CRYSTAL STRUCTURE OF 6-O-p-BROMOBENZOYL ZEORIN

T.Nakanishi, H.Yamauchi, T.Fujiwara and K.Tomita
Faculty of Pharmaceutical Sciences, Osaka University
Toneyama, Toyonaka, Osaka, Japan

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As described in the previous paper, the stereostructure of leucotylin (I), $C_{30}H_{52}O_3$, a triterpenoid isolated from a lichen Parmelia leucotyliza Nyl., was determined on the basis of chemical[1] and X-ray[2] investigations.

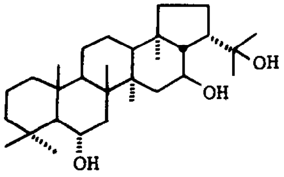
On the other hand, the stereostructure of zeorin, $C_{30}H_{52}O_2$, mp. 228-229°, which is a widely distributed triterpenoid in the lichen family, has been proposed as (II) with C_{21}-β-isopropanol group under the chemical correlation with leucotylin (I).[3]

The configurational difference at C_{21}-position between leucotylin and zeorin is quite remarkable from a biogenetic standpoint, considering that the both triterpenoids have been generally found to coexist in the lichen family.

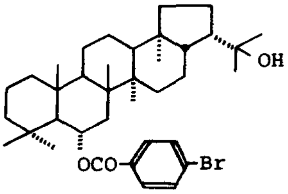
In order to investigate the above interesting point and also to substanciate the proposed configuration at C_{21}- and C_{17}-positions, 6-O-p-bromobenzoyl zeorin (III), a derivative of zeorin, has been used for the X-ray diffraction study.

The bromine derivative (III), $C_{37}H_{55}O_3Br$, mp.224-227°, IR(CCl_4, cm^{-1}):3607, 1715,1588,1274; NMR(100Mc, τ in $CDCl_3$):9.25(3H),9.16(3H),9.03(6H),8.98(3H), 8.87(6H),8.83(3H), all singlet; 4.52(1H,multiplet); 2.50,2.16(4H,A_2B_2 type quartet), was obtained by bromobenzoylation of zeorin with p-bromobenzoyl chloride and pyridine. The retention of carbon skeleton during the derivation was secured by recovering zeorin on alkaline hydrolysis of the bromobenzoyl derivative (III).

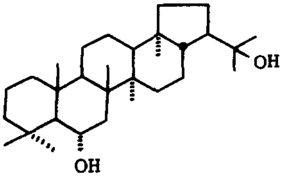
The crystals of (III) were recrystallized in benzene-acetone as colorless needles elongated along the b-axis. By oscillation and Weissenberg photographs taken with Cu Kα radiation, it was shown that this crystal is ortho-



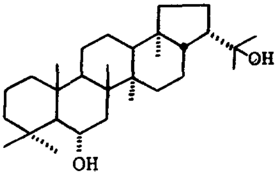
(I) leucotylin



(III) 6-O-p-bromobenzoyl zeorin



(II) zeorin (incorrect)



(IV) zeorin (correct)

rhombic with four molecules per unit cell of dimensions and space group as: a = 17.34 ± 0.04, b = 29.55 ± 0.01, c = 6.69 ± 0.01 Å, and $P2_12_12_1$. The density, 1.26 g/cc., was measured by the flotation method in a calcium chloride aqueous solution. Three-dimensional intensity data around the a- and the c-axes were recorded on multiple film equi-inclination Weissenberg photographs with Cu Kα radiation, and the intensities of 1720 independent reflections were estimated by visual comparison with a standard scale, and converted to $|F_o|^2$ after correction of Lorentz and polarization factors. The approximate scaling factor and overall temperature factor(B=7.65) were determined by Wilson's method. The structure determination was initiated by usual heavy atom method, and the bromine atom position (0.250, 0.048, 0.000) was determined from the three-dimensional Patterson synthesis. The first Fourier synthesis using the phase based on the bromine atom position was calculated, but it was not successful to find any plausible molecular structure because of the appearance of extra-mirror planes owing to the special location of bromine atom. The next attempt to solve the structure was carried out by application of the minimum function, which revealed the reasonable peak heights for the molecular skele-

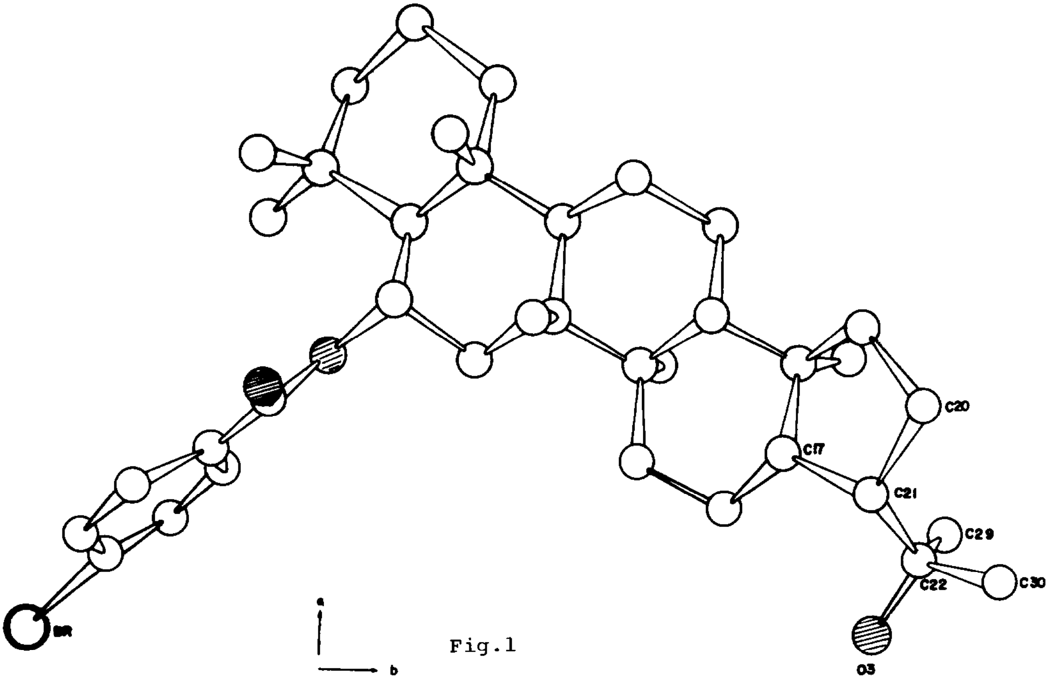

C20
C17
C21
C29
C22
C30
O3
BR
a
b

Fig.1

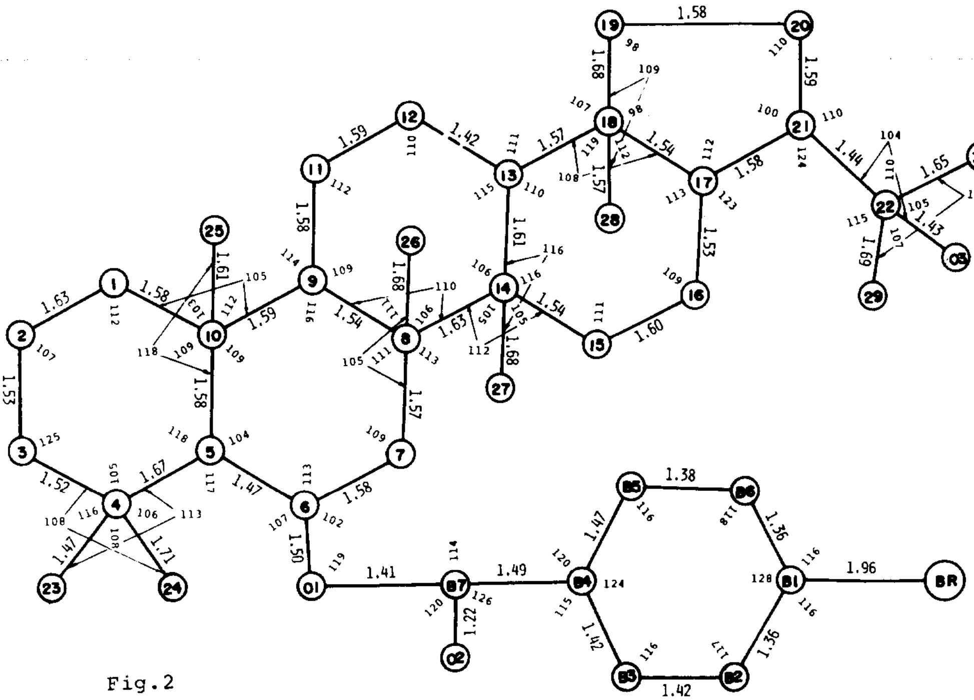

19
20
1.58
1.68
1.59
18
21
12
1.42
13
1.57
1.54
17
1.58
1.44
22
1.65
30
1.43
O3
1.69
29
11
1.59
1.58
28
1.61
16
1.53
15
1.60
14
1.54
27
1.68
26
1.68
8
1.63
9
1.54
10
1.59
25
1.61
1
1.58
2
1.63
1.53
3
1.58
5
7
1.57
4
1.52
1.67
6
1.47
1.58
23
1.47
24
1.71
1.50
O1
1.41
B7
1.22
O2
1.49
B4
B5
1.47
1.38
B6
1.36
B1
1.96
BR
B3
1.42
B2
1.42
1.36

Fig.2

ton. The molecular structure of 6-O-p-bromobenzoyl zeorin (III) was entirely determined by the successive three-dimensional Fourier synthesis.

The residual, R-factor, at this stage was 0.28. Refinement of the structural parameters was carried out by the block diagonal least squares method.

After four cycles refinements with isotropic temperature factor and two cycles with anisotropic temperature factor for all nonhydrogen atoms, the R-factor was dropped to 0.12. The molecular configuration viewed down through the c- axis are shown in Fig.1. The bond lengths and angles are shown in Fig.2, in which some bond lengths are longer or shorter than the normal values, however, the maximum standard deviation of bond length is 0.07Å and no further discussion on bond lengths will be undertaken here.

The result of X-ray analysis on the molecular structure of 6-O-p-bromobenzoyl zeorin (III) indicates that zeorin should have α-oriented isopropanol side-chain at C_{21}-position and the trans-fused D/E junction. Furthermore, it is of particular interest that the conformation of E-ring in (III) is "envelope" form as similar as hopane derivative$^{4)}$, whereas it is "half-chair" form in leucotylin derivative$^{2)}$. Consequently, the structure of zeorin should be revised as (IV) with C-21βH which is contrary to the proposed structure (II). Further chemical experiments are now established and it is reported in the following paper.

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