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X-RAY ANALYSIS OF BETULAFOLIENETETRAOL OXIDE, A TRITERPENE ISOLATED FROM BETULA COSTATA TRAUTV.

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Summary: The structure of betulafolienetetraol oxide has been established by X-ray analysis as 20(S),24(R)-epoxydammar-3α,12β,17α,25-tetraol.

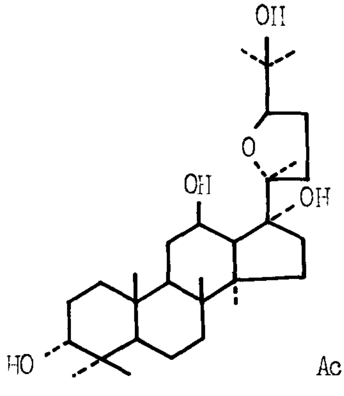
Recently we reported[1] the isolation of a new triterpene from leaves of Far East birch _Betula costata_ Trautv. The structure of betulafolienetetraol oxide (I) was assigned to it on the basis of chemical and spectroscopic studies. To complete elucidation of the structure and side chain stereochemistry, the X-ray analysis of I has been carried out. The analysis of I showed that it has the structure of 20(S),24(R)-epoxydammar-3α,12β,17α,25-tetraol.
Crystal data: $C_{30}H_{52}O_5$, M = 492. Orthorhombic, a = 11.605(2), b = 15.565(4), c = 15.595(4) Å, V = 2817(1) Å^3. Space group $P2_12_12_1$, Z = 4, D_c = 1.16 g/cm^3.

Crystals of I were grown from acetone solution. The crystal used for data collection was approximately 0.50 x 0.30 x 0.35 mm. Intensities of 2597 independent reflections with 2θ to 50° were obtained by θ-2θ scanning technique on a "Syntex $P2_1$" diffractometer (Mo Kα-radiation, graphite monochromator). 1445 reflections with $I \geq 1.96\sigma$ were used in the analysis.

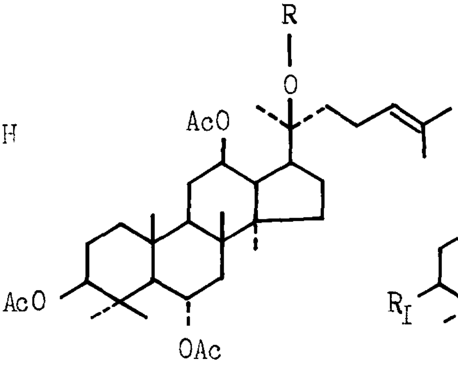
The data were corrected for Lorentz-polarization effects, placed on an absolute scale by Wilson's method and converted into normalized structure factors.

The structure was solved by direct method. Four variants of phases of 284 reflections with $E \geq 1.45$ were computed by MULTAN (E-XTL) program. The variant with the highest figures of merit resulted in an E-map in which 32 of the 35 non-hydrogen atoms could be located. Successive Fourier synthesis defined the remaining C and O atoms. Coordinates of 50 H-atoms were determined using the difference synthesis. A location of H-atoms linked with O(3) and O(12) was not possible to determine by synthesis.

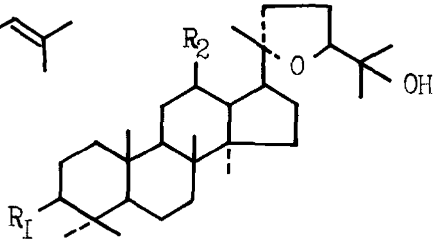
The structure was refined by full-matrix least-squares technique inclu-



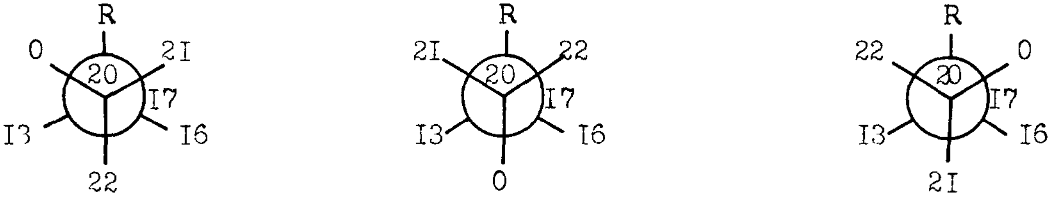
I



II: R=tetra-Ac-β-D-glucose



III: $R_1=R_2$=-O-p-brombenzoyl



A B C

A,B,C: R=H,OH

ding anisotropic thermal parameters of non-hydrogen atoms and fixed-hydrogen atoms to R = 0.074 for the 1445 observed reflections.[+]

The conformation of I and the intramolecular hydrogen bonds are shown in Fig.1. The distance from H-atom of hydroxyl group at C(17) to the atom O(20) is equal to 2.31 Å. Such a distance shows the weak hydrogen bond between the hydroxyl group and the oxygen of tetrahydrofurane ring. The hydrogen bond O(25) - H ... O(12), stabilizing the position of isopropanol group at C(24), is stronger. The distance H...O(12) is 1.96 Å. Based on the O...O distances shown in Fig.1 the bond O(12) - H ... O(20) seems to be the strongest of all the hydrogen bonds. This H-bond stabilizes the conformation A of the side chain. It is impossible in the other two conformations, because the distance O(12)...O(20) in conformation B even is equal to 4.23 Å, as it has been shown by X-ray analysis of panaxoside A progenin I acetate[2] (II). On acetylation of hydroxyl group at C(12) of compounds with the open side chain, having atom O(20), the side chain turns into conformation B, which is confirmed by the X-ray analysis of II. At the similar substitution of compounds with the closed side chain, the side chain, as a result of rotation about the bond C(17)-C(20), turns into conformation C, which is confirmed by the X-ray analysis of 3β,12β-O-di-p-brombenzoylpyxinole[3] (III).

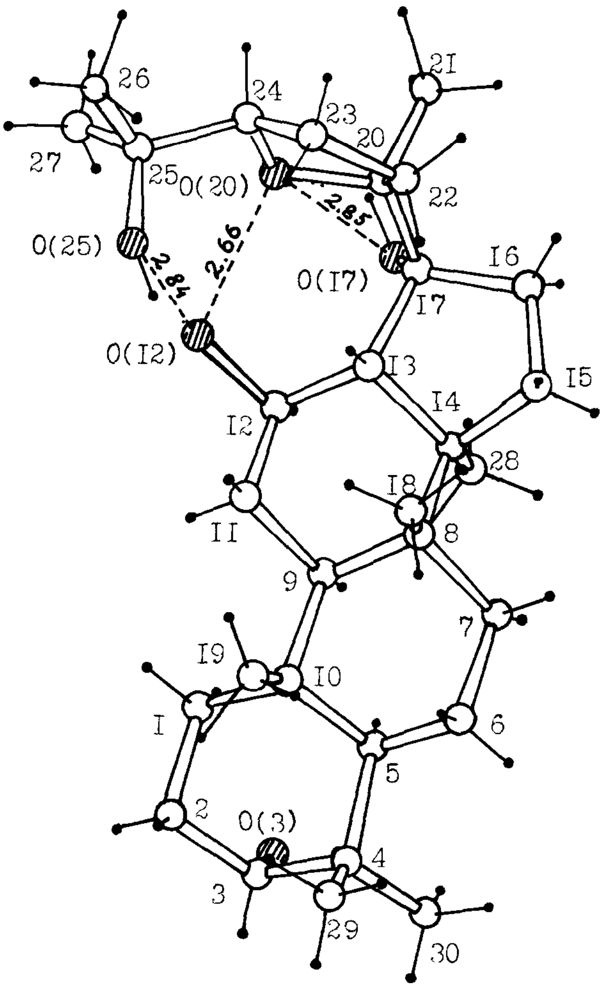


Figure 1. Conformation of I and intramolecular H-bonds. The view along the a-axis.

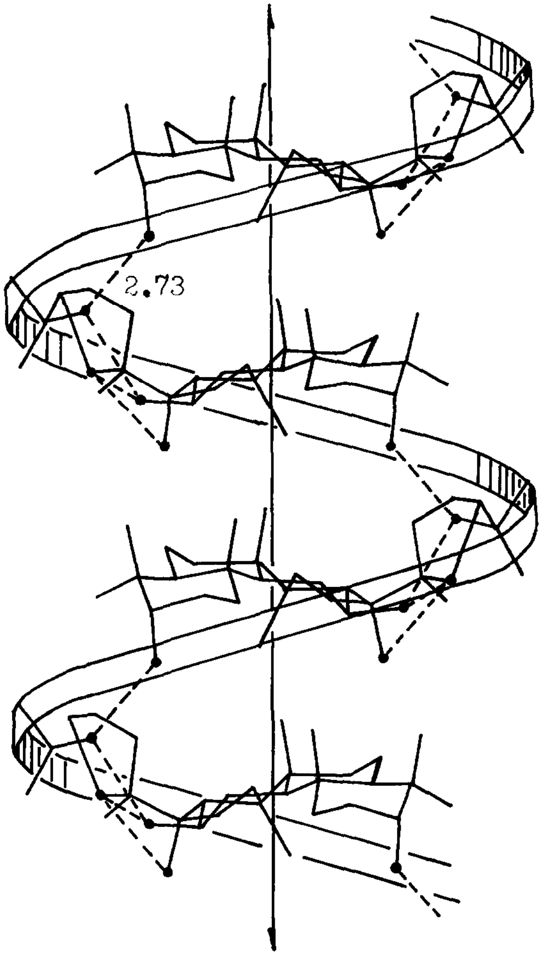


Figure 2. Molecular packing. The view along the c-axis.

Molecules of I are packed in the crystal in coils (Fig. 2), in which the dominant plane of a molecule is perpendicular to a screw axis (crystallographic a-axis). The molecules are bonded with the intermolecular H-bonds O(3) - H ... O(25). The O...O distance corresponding to H-bond is equal to 2.73 Å.

The similarity of OH - bands frequency values of IR - spectra of the I solution in CHCl$_3$: 3300, 3405 (disappears when diluted), 3426, 3581, 3611 cm^{-1} and crystals of I (nujol): 3310, 3372, 3457, 3590, 3607 cm^{-1} indicates to the conservation of all the hydrogen bonds and, consequently, the conformation of I at the crystal - solution transition.

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2. S.G.Ilyin, A.K.Dzizenko, G.B.Elyakov, B.L.Tarnopolsky and Z.S.Safina, Tetrahedron Lett., 593 (1978)
3. H.Yamauchi, T.Fujiwara and K.Tomita, Tetrahedron Lett., 4245 (1969)

[+] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, (England) [see Tetrahedron Letters, 3081 (1978)]

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