Tetrahedron Letters No.37, pp. 2599-2601, 1964. Pergamon Press Ltd.
Printed in Great Britain.

THE CONSTITUTION AND ABSOLUTE STEREOCHEMISTRY OF SWIETENINE

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(Received 13 July 1964)

We have determined the crystal structure of the p-iodobenzoate of destigloylswietenine and hence defined the molecular structure of swietenine,[1] $C_{32}H_{40}O_9$, a constituent of Swietenia macrophylla, as (I; R = tigloyl). The absolute stereochemistry shown was deduced by Bijvoet's anomalous-dispersion method.[2]

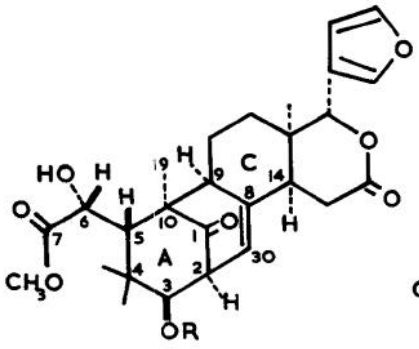
The p-iodobenzoate[3] crystallizes in the orthorhombic system, space group $P2_12_12_1$, with four molecules of $C_{34}H_{37}O_9I$ in a unit cell of dimensions a = 17.44, b = 16.36, c = 11.20 Å. From equi-inclination Weissenberg photographs 1534 independent structure amplitudes were evaluated. The co-ordinates of the iodine atom were obtained from a Patterson synthesis and yielded a first set of structure factors for which the value of R, the average discrepancy between observed and calculated structure amplitudes, was 37.4%.

In the first Fourier synthesis the δ-lactone, the adjoining ring C and ring A with some of its substituents were located initially. In our search for further molecular detail we were influenced

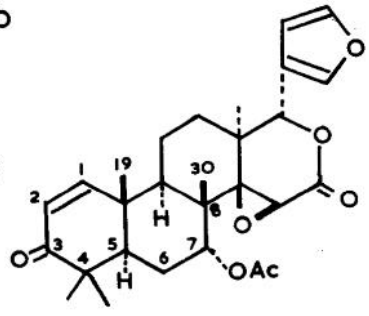
by the suspected biogenetic relationship of swietenine to the limonin[4] group of triterpenoids, e.g. gedunin (II),[5] and were therefore troubled by the α-orientation of the 19-methyl group and by the position of the hydroxy ester and gem-dimethyl groups. We eventually realized that these features could be explained by cleavage of the 7-8 bond in a molecule of the gedunin type, followed by rotation of ring A about the 9-10 bond with addition of C(2) to C(30). Thereafter the location of the remaining atoms was straightforward and structure (I; R = p-IC_6H_4CO) was deduced for the derivative. When the carbon and oxygen atoms (all weighted as carbon) were included with the iodine atom in the calculation of a second set of structure factors the value of R was 20.8%. After a round of Fourier refinement the light atoms were assigned their correct chemical types in the subsequent structure-factor calculation and the value of R was 18.2%. Further refinement is continuing.

The position of the double bond between C(8) and C(30) was established by the coplanar arrangement of carbon atoms 2, 30, 8, 9 and 14.

The chemistry of swietenine is discussed in the accompanying communication.[3]



(I)



(II)

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