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THE CRYSTAL STRUCTURE ANALYSIS OF OBTUSIFOLIN

$C_{24}H_{22}O_7$, A FLAVANONE

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From the overground parts of Gnaphalium obtusifolium (Compositae) a flavanone, Obtusifolin $C_{24}H_{22}O_7$, together with three more lipophilic substances was isolated by Prof. R. Hänsel et al (1) and kindly supplied to us. The purpose of the present investigation was to elucidate the correct crystal and molecular structure of this natural product.

Colourless clear crystals (m.p. 202-204°C) were crystallized from acetone. The crystallographic data are: $a = 20.96$, $b = 12.47$, $c = 7.99$ Å; $d_m = 1.32$ gcm^{-3}, $d_{cal} = 1.34$ gcm^{-3}. The space group is $P2_12_12_1$; $Z = 4$.

The three-dimensional X-ray diffraction intensities were measured on a Siemens off-line four-circle Diffractometer, using CuKα radiation. All the reflections with $\Theta \leq 64°$ were measured (mode of measurement: $\Theta/2\Theta$ scan, 5-point measuring procedure). Of 1926 reflections observed, 167 reflections were too weak to be measured. The structure was solved by a direct method (2, 3, 4), programmed by one of us, which does not require any initial information about the stereochemistry of the molecule. This procedure is based on a cyclic application of the statistical triple product phase relationships (5) and the Sayre equation (6).

The free choice of the origin in the unit cell and of either of the two enantiomorphic structures allows the phases of four two-dimensional reflections to be arbitrarily fixed in the space group concerned here. For the analysis of the present structure, however, three of the four starting reflections were three-dimensional. The phases of these three-dimensional reflections were continually refined during the cyclic procedure (see also (4)). In order to extend the initial phase set two more two-dimensional reflections were included. All the four resulting phase sets were cycled until the phases of all the unitary structure factors used (300 reflections) were determined. U-Fourier syntheses of the first two sets, selected by the best Q-criteria, did not lead to the correct solution of the structure. A subsequent U-Fourier synthesis of the third best set (having 292 reflections of high values out of cycled 300 reflections), revealed 29 out of 31 non-hydrogen atoms of the molecule immediately, 24 of them were picked by their high electron density values and the remaining 5 were fixed by electron density and bondlength

considerations. A Fourier synthesis using all the 1926 phases calculated from the positions of these 29 atoms yielded the remaining two atoms. The position of the outer laying carbon atom of the ethyl group is spread over a region; the spread might be due to the statistical position of this group, because of which the C-C bondlength is 1.24 Å, less than the normal value, 1.54 Å, and also the temperature factors of the atoms in this group are high. Using isotropic and anisotropic refinements and difference Fourier syntheses, the positions of 15 hydrogen atoms could be located, yielding an R-index of 7.9 %. Figures la, lb show the Obtusifolin molecule in the x, y-projection. Obtusifolin is a dihydroxyflavanone which is linked with a trisubstituted 4-hydroxy-pyron-2-ring by a methylene bridge (Fig. 2).

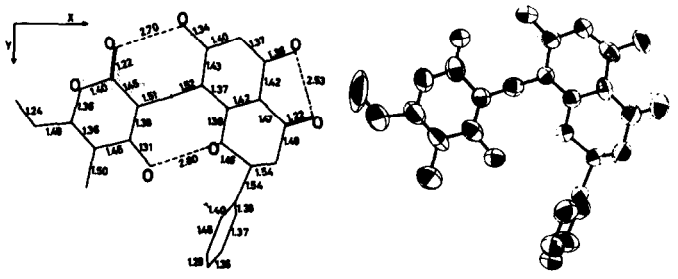

Fig. la, lb, Molecule Obtusifolin with bondlengthsin the x, y-projection

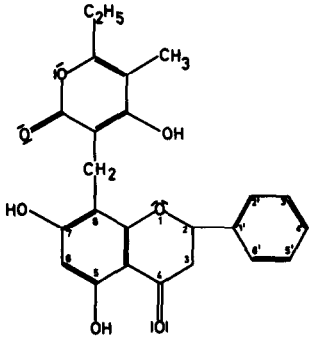

Fig. 2, Structural formula of the molecule Obtusifolin

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