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Stellatic Acid: a New Class of Sesterterpenoid; X-Ray Crystal Structure

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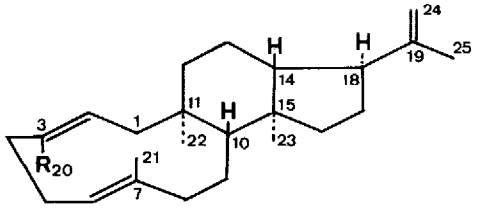
Summary : *The complete structure of a unique tricyclic sesterterpene, stellatic acid, was established by X-ray diffraction of its p-bromophenacyl ester.*

In the course of the study on the metabolites of *Aspergillus stellatus* Curzi (IMI No: 112543) cultivated in ordinary Czapak-Dox medium, 100 mg of an acidic compound was isolated besides the so far reported five xanthones [1] [2] from petroleum ether extract of 550 g of dried mycellium.



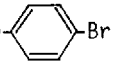
1. R = COOH
2. R = $COOCH_2CO$- 
3. R = CH_3

Figure 1

The acid was thus designated as stellatic acid (1), $C_{25}H_{38}O_2$, m.p. 224° (from benzene), *m/e* 370 (M^+, 37 %), 355 (26 %, 370-CH_3), 326 (26 %, 370-CO_2), 189 (100 %, 355-$C_{10}H_{14}O_2$); $[\alpha]_D^{25}$ +13.5° (*c* 0.3, $CHCl_3$); λ_{max} (ethanol) 223 nm (ε 8500), characteristic of αβ-unsaturated carboxylic acid; ν_{max} ($CHCl_3$) 3600-2400 broad, 1675 cm^{-1}, indicating the presence of αβ-unsaturated carboxylic acid group, 875 cm^{-1}, due to exomethylene group; ^{1}H-n.m.r. ($CDCl_3$) two olefinic protons (σ 5.90 and 4.91, each as *dd*), exomethylene protons (σ 4.70, *s*), four methyl signals (σ 1.72, 1.31, 0.88 and 0.82, each as *s*); ^{13}C-n.m.r. ($CDCl_3$) acyl carbon (σ 171.3, *s*), six alkenic carbons (σ 159.0, 148.0, 139.6, 125.3, 123.7 and 109.6, as *d*, *s*, *s*, *s*, *d* and *t*, respectively). These data suggested the structure of 1 to be a tricyclic sesterterpenoid acid. The detailed structure as well as the relative and absolute stereochemistry of this compound were established by X-ray diffraction of its *p*-bromophenacyl ester (2).

The crystals were grown in a hexane solution as colorless prisms elongated along *b* axis. The lattice parameters and intensity data were measured on a Philips four-circle X-ray diffractometer using Cu*K*α radiation monochromated by a graphite plate. The size of the crystal was about 0.05 x 0.1 x 0.25 mm. Crystal data: $C_{33}H_{38}O_3Br$, m.p. 135°, M=567.6, monoclinic, space group $P2_1$, Z=2, a=20.064 (10), b=6.712 (3), c=11.258 (6) Å, β=101.77 (4)°, V=1484.2 Å^3. μ for Cu*K*α=10.6 cm^{-1} Dx=1.270 gcm^{-3}. Intensities of 2234 *hkl* reflections were measured along with 865 *hk̄l* Friedel reflections within the 2θ angle of 6°~156°. The crystal structure was determined by the anomalous dispersion method as had been used in a previous work [3], which gave the absolute configuration of the molecule at the same time. Refinement of the atomic parameters for 37 heavier atoms (C, O and Br) were carried out by the method of block-diagonal least squares. The R value decreased to 0.08 for 2234 structure factors. No attempt has been made to locate hydrogen atoms.

The structure of the molecule is illustrated in Figure 2 by an *ORTEP* drawing [4].

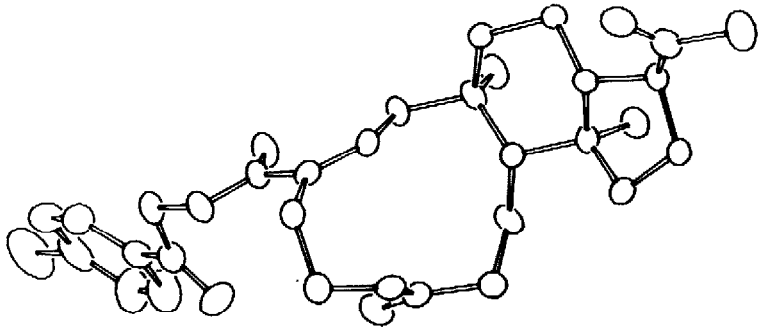


Figure 2

Stellatic acid was thus found to be the first example of a biogenetically new class of sesterterpenoid with a unique skeletal structure composed of a 11-6-5 membered tricyclic system, and it should presumably be derived from the assumed precursor 3 which is expected as the primary cyclization product of this class from all *trans* geranylfarnesyl pyrophosphate.

REFFERENCES

[1] a) A. Kamal, S. A. Husain, R. Noorani, N. Murtaza, I. H. Qureshi and A. A. Qureshi, *Pakistan J. Sci. Ind. Res.*, 13, 251 (1970). b) A.Kamal, S. A. Husain and A. A. Qureshi, *ibid.*, 90, 104 (1971).

[2] Among the metabolites of *Aspergillus variecolor* two xanthones are common with those obtained from *Aspergillus stellatus* and their structures were revised: K. K. Chexal, C. Fouwether, J. S. E. Holker, T. J. Simpson and K. Young, *J. chem. Soc., Perkin I*, 1548 (1974).

[3] Y.Iitaka, H. Nakamura, K. Takada and T. Takita, *Acta Cryst.*, B30, 2817 (1974).

[4] C. k. Johnson, *ORTEP. Report* ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1965).

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