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THE ABSOLUTE CONFIGURATION OF ASSUFULVENAL*

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Key Word Index—*Joannesia princeps*; Euphorbiaceae; assufulvenal; bis-sesquiterpene; absolute configuration; X-ray crystal structure.

Abstract—The absolute configuration of assufulvenal [(10*R*)-3-((10*R*,*E*)-1*β*,11-cycloguai-4-en-15-ylidene)-guaia-1,4,11-trien-15-al], a novel pigment from the root bark of *Joannesia princeps* was determined by multiple scattering X-ray experiments. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

In the course of a phytochemical examination of the medicinal plant *Joannesia princeps* (Euphorbiaceae), we isolated as a minor pigment the novel fulvenic bis-sesquiterpene assufulvenal (**1**) [2]. Corresponding 'monomeric' cycloguaienes have been found among the major plant constituents and are responsible for the biological activity of the plant [3].

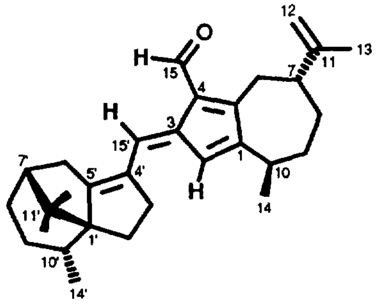
The basic structure and relative configuration of **1** was determined spectroscopically, and X-ray crystallographic analysis helped to reveal its relative configuration [2]. We now report on multiple scattering X-ray experiments [4] which established the absolute configuration of **1**.

RESULTS AND DISCUSSION

Assufulvenal (**1**), $C_{30}H_{40}O$, $[\alpha]_D^{21}$ -171°, was isolated from the root bark of African and Brazilian *Joannesia princeps* [2].

Crystals suitable for X-ray measurements were grown from a dichloromethane/ethanol mixture. The absolute configuration was determined from the crystallographic measurements by means of triplet phases [5], and the result is shown in the projection of the molecule by displacement ellipsoids (Fig. 1).

The X-ray method applied is useful for structures which contain only light atoms like **1** [6, 7]. In these cases the absence of heavier atoms makes a determination of the absolute configuration by Bijvoet differences nearly impossible.



EXPERIMENTAL

The structure factor moduli and phases, which derived from the absolute coordinates and which are necessary to calculate suitable triplet relations, came from the X-ray studies of the relative configuration [2].

A total of 14 pairs of triplet phases was measured and they all were without contradiction. Table 1 compiles the structure factors and their phases used for the six examples of triplet phase pairs presented in Table 2. The diagrams of Table 2, whose basic lines are indicated by 1.000, show the changes of the recorded intensities. All results are in agreement with the triplet phases calculated on the basis of the refined atomic coordinates.

The experiments were performed with a six-circle-diffractometer [8] installed at a rotating anode generator with Cu-Kα1 radiation.

All crystallographic details are deposited with the Cambridge Crystallographic Data Center.

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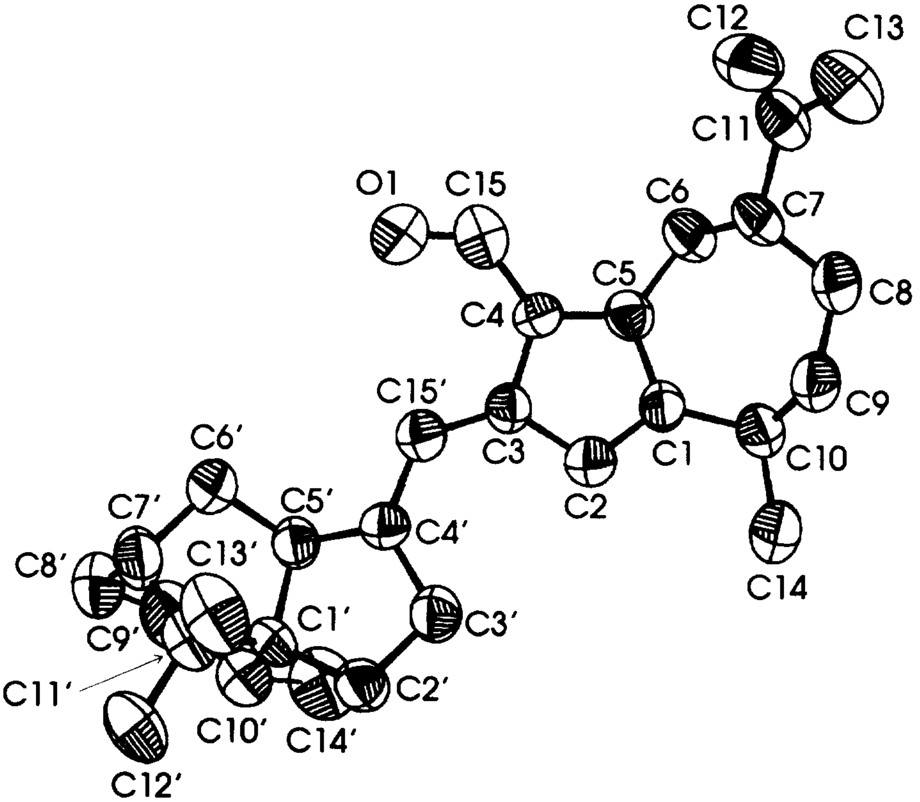
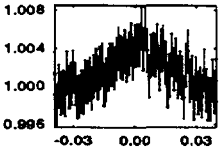
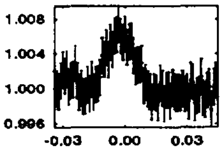
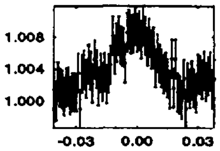
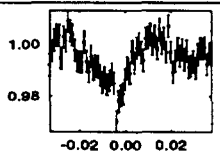
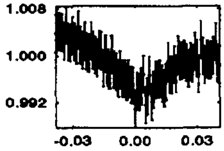
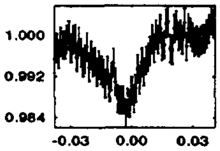


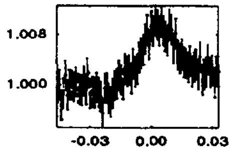
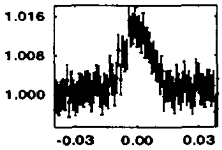
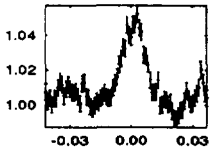
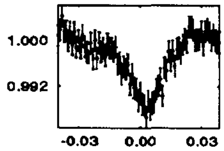
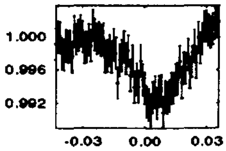
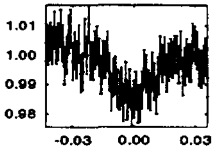
Fig. 1. Projection of the molecule with anisotropic displacement ellipsoids.

Table 1. Structure factor data used for the determination of the absolute structure of **1**

hkl	F_{obs}	ϕ_{cal}
124	27.7	−30°
245	56.3	83°
040	24.3	180°
144	32.2	99°
221	36.6	137°
121	51.4	98°
231	48.9	114
132	51.0	−136°
313	48.9	−62°
211	29.2	−124°
301	38.4	−90°

Table 2. Triplets used for the determination of the absolute structure of **1**

Triplett	$\underline{h}$	ϕ_i	$\underline{h}$	ϕ_i	$\underline{h}$	ϕ_i
-h -k -l	$\bar{1}\bar{2}\bar{4}$	30°	$\bar{1}\bar{4}\bar{4}$	-99°	$0\bar{4}0$	180°
h′ k′ l′	$\bar{2}11$	-56°	$30\bar{1}$	90°	$\bar{2}2\bar{1}$	-43°
h″ k″ l″	313	-62°	$\bar{2}45$	-83°	221	137°
$\Phi = \sum_i \phi_i$	$\Phi_1^+ = -88°$		$\Phi_2^+ = -92°$		$\Phi_3^+ = -86°$	
						
-h -k -l	124	-30°	144	99°	040	180°
h′ k′ l′	$2\bar{1}\bar{1}$	56°	$\bar{3}01$	-90°	$2\bar{2}1$	43°
h″ k″ l″	$\bar{3}\bar{1}\bar{3}$	62°	$2\bar{4}\bar{5}$	83°	$\bar{2}\bar{2}\bar{1}$	-137°
$\Phi = \sum_i \phi_i$	$\Phi_1^+ = 88°$		$\Phi_2^+ = 92°$		$\Phi_3^+ = 86°$	
						

Triplett	$\underline{h}$	ϕ_i	$\underline{h}$	ϕ_i	$\underline{h}$	ϕ_i
-h -k -l	$\bar{1}\bar{4}\bar{4}$	-99°	$0\bar{4}0$	180°	$\bar{2}\bar{1}\bar{1}$	124°
h′ k′ l′	$\bar{2}31$	66°	221	137°	$1\bar{2}\bar{1}$	-82°
h″ k″ l″	313	-62°	$\bar{2}2\bar{1}$	-43°	132	-136°
$\Phi = \sum_i \phi_i$	$\Phi_1^+ = -95°$		$\Phi_2^+ = -86°$		$\Phi_3^+ = -94°$	
						
-h -k -l	144	99°	040	180°	211	-124°
h′ k′ l′	$2\bar{3}\bar{1}$	-66°	$\bar{2}\bar{2}\bar{1}$	-137°	$\bar{1}21$	82°
h″ k″ l″	$\bar{3}\bar{1}\bar{3}$	62°	$2\bar{2}1$	43°	$\bar{1}\bar{3}\bar{2}$	136°
$\Phi = \sum_i \phi_i$	$\Phi_1^+ = 95°$		$\Phi_2^+ = 86°$		$\Phi_3^+ = 94°$	
						

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