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G. J. Chintalwar, V. R. Mamdapur, V. S. Yadava, and V. M. Pmdmanabhan

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THE CRYSTAL AND MOLECULAR STRUCTURE OF A GUAIANOLIDE FROM *CYATHOCLINE PURPUREA*

G.J. CHINTALWAR, V.R. MAMDAPUR,*

Bio-Organic Division

V.S. YADAVA, and V.M. PMDMANABHAN

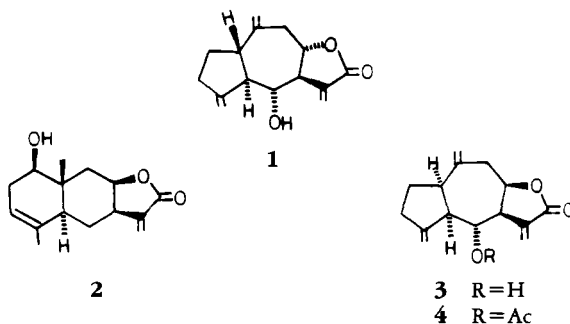
Solid State Physics Division, Bhabha Atomic Research Centre, Bombay 400 085, India

ABSTRACT.—The structure of a guaianolide isolated from *Cyathocline purpurea* was established as 6- α -hydroxy-4(14), 10(15)-guaianolide [**1**] spectroscopically and confirmed by X-ray analysis.

Very little work has been reported on phytochemistry of the common plant *Cyathocline purpurea* (Asteraceae) (1,2). There are no published reports of biological studies nor of isolation of any crystalline constituents from this species. Herein we report for the first time isolation of a colorless crystalline compound with plant growth regulatory (PGR) activity from *C. purpurea*. In our preliminary screening for naturally occurring bioactive compounds, we found that the petroleum ether extract of aerial parts of *C. purpurea* exhibited PGR activity. Extensive cc followed by preparative tlc and crystallization resulted in isolation of **1**, mp 118°, the active principle responsible for plant growth regulation. The known eudesmanolide **2** and guaianolide **3** were identified via their respective derivatives or regeneration from the gummy material obtained after repeated cc of the Me₂CO extract of *C. purpurea* (2). Nagasmpagi *et al.* (2) established the configuration of sesquiterpenoids based on spectral data particu-

larly on chemical shift and couplings. The present paper deals with the isolation and complete structural determination of the PGR active principle of *C. purpurea* by spectral data and X-ray crystallography.

Kalsi *et al.* (3) have shown that some of the sesquiterpene lactones with a conjugated methylenic double bond, trisubstituted double bond, or a cyclopropane ring exhibited PGR activity. These reports (2,3) suggested that our crystalline compound **1** could belong to the class of sesquiterpene- γ -lactones. This was further established by spectroscopic data. Compound **1** showed ir bands at 3450 and 885 cm⁻¹, suggesting the presence of hydroxyl and exocyclic methylene functions, respectively. The ir band at 1770 cm⁻¹ and uv absorption at 208 nm supported the presence of an α -methylene- γ -lactone ring. Its ¹³C nmr, ms, and elemental analysis further suggested that the compound **1** has the molecular formula C₁₅H₁₈O₃. The ms of the completely hydrogenated



product, $C_{15}H_{24}O_3$, showed $[M]^+$ at m/z 252. This suggested the presence of three $-C=C-$ in the parent compound. The 1H -nmr signals at δ 6.2, 5.05, 4.95, 4.38, 3.67, and 3.17 suggested the presence of the guaianolide skeleton (2,4,5) with two isolated exocyclic methylene groups and a conjugated methylene group. The signal at δ 3.68 supported the presence of a secondary hydroxyl group. These data were in close agreement with the guaianolide acetate (2), except for the acetate's proton signals. The spectroscopic data of the acetate derivative of **1** were in good agreement with the reported acetate **4** (2). Hence, these spectroscopic data suggested that the structure of the parent alcohol could be **3**. However, the difficulties in oxidation of the secondary hydroxyl group to a ketone and poor yield of acetate formation even under modified conditions led us to ascertain its structure by X-ray analysis. The structure and configuration were determined by X-ray crystallography.

A single crystal X-ray analysis unequivocally confirmed the structure of the guaianolide as 6- α -hydroxy-4(14), 10(15)-guaianolide [**1**]. A computer-generated PLUTO diagram of **1** is shown in Figure 1. Full-matrix least squares refinement of atomic positions and thermal parameters converged to $R = 0.074$, for 1515 reflections measured with a four-circle diffractometer.

Final non-hydrogen atom positional and thermal parameters are given in Table 1. The analysis revealed that bond lengths all lie close to accepted values. The cycloheptane ring is in twist conformation. The cyclopentane ring adopts a half-chair conformation ($\Delta C_2 = 6.6^\circ$), and the γ -lactone ring also has half-chair conformation on the twist axis ($\Delta C_2 = 2.0^\circ$). Both the five-membered rings are trans fused to a seven-membered ring. Hence, the structure established is as shown in **1**.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Ir spectra were recorded on a Perkin-Elmer 137B and are in cm^{-1} . Uv spectra were run on a Zeiss RPQ-20A spectrometer. 1H nmr was scanned on JEOL 270 MHz and ^{13}C nmr on Bruker HM 500 MHz FT spectrometer with TMS as internal standard and reported in δ ppm. Eims analysis was carried out on a VG MICROMASS 7070 F instrument and cims on a VGU-Mass 7070 H instrument. Optical rotations were recorded on Perkin-Elmer model 141 polarimeter.

ISOLATION PROCEDURE.—Fresh plants of *C. purpurea* were collected around the Anushaktinagar area, Bombay, India, during September and identified by Dr. V. Abraham, Bhabha Atomic Research Centre. A voucher specimen (No. 413) has been deposited in the herbarium of the Landscape and Cosmetic Maintenance Section, BARC. The aerial part (1 kg) on Soxhlet extraction with distilled petroleum ether (60–80°) followed by removal of solvent under reduced pressure gave a thick oil. This was subjected to elaborate cc over alumina (neutral, Grade III, solvent petroleum ether/ Et_2O). Fractions were eluted with petroleum ether/ Et_2O (10, 20, 30,

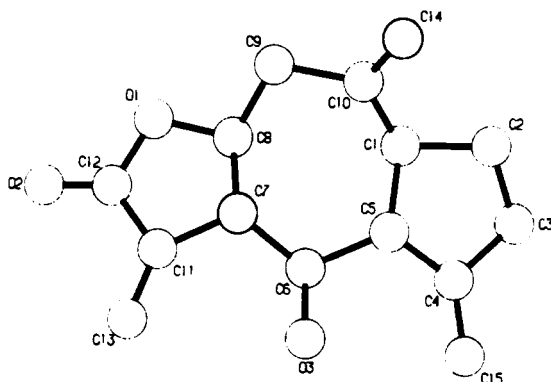


FIGURE 1. Structure and solid-state configuration of **1**.

TABLE 1. Fractional Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) for Compound 1.

Atom	x	y	z	UEQ
C-1	-12354(7)	5866(00)	-1403(11)	76
C-2	-13240(7)	5996(36)	-1421(13)	99
C-3	-13614(8)	6628(36)	-2476(12)	94
C-4	-13027(8)	8484(33)	-2749(75)	75
C-5	-12300(8)	8218(30)	-2019(10)	65
C-6	-11561(8)	8402(31)	-2509(11)	70
C-7	-10800(7)	7793(27)	-1774(10)	56
C-8	-10745(8)	5216(29)	-1385(11)	66
C-9	-10997(8)	4732(29)	-0398(10)	68
C-10	-11852(8)	5600(35)	-0443(11)	82
C-11	-10093(8)	7971(31)	-2242(11)	72
C-12	-9626(8)	5991(44)	-1830(14)	99
C-13	-9862(10)	9660(34)	-2812(12)	95
C-14	-12095(9)	6031(40)	-0381(11)	104
C-15	-13206(10)	10062(37)	-3478(14)	108
O-1	-9974(6)	4458(26)	-1287(9)	106
O-2	-8993(6)	5534(31)	-1940(10)	141
O-3	-11569(5)	10767(21)	-2878(7)	81

40, 50% successively). Evaporation of the fraction from petroleum ether-Et₂O (70:30) gave a solid which was subjected to preparative tlc (Si gel, CHCl₃). The major band, which was located by viewing under uv light ($R_f = 0.5$), was scraped off and eluted with CHCl₃. Removal of solvent followed by crystallization of residue furnished a pure colorless compound **1**: mp 118°; yield 0.02%; uv λ max (EtOH) 208 nm; ir cm⁻¹ 3450, 3000, 1770, 1460, 1390, 1240, 1140, 1040, 990, 910, 885; ¹H nmr 1.71 (dddd), 1.84 (dddd), 2.47 (m), 2.42 (m), 2.62 (dd), 2.83 (dddd), 3.19 and 3.15 (d), 3.65 (dddd), 4.38 (dddd), 4.95 (d), 5.05 (s), 6.28 (dd); ¹³C nmr 29.42 (t), 33.32 (t), 45.22 (dd), 53.03 (d), 58.01 (d), 74.55 (d), 76.63 (d), 108.67 (t), 111.2 (t), 124.6 (t), 137.7 (s), 152.47 (s), 170 (s, C=O); cims m/z [M + 1]⁺ 247, 229, 210, 183, 79; [α]²⁵ (CHCl₃) 589/-76.7, 546/-84.1, 436/-147.1. Found C 73.27, H 7.51; required for C₁₅H₁₈O₃, C 73.17, H 7.48%. Complete hydrogenation of **1** with 10% Pd/C in EtOH gave a product, [M]⁺ 252.

X-RAY STRUCTURE DETERMINATION.¹—Compound **1** crystallizes in monoclinic space

group. The crystal data are: space group $P2_1$, $a = 17.772$ (8), $b = 5.619$ (4), $c = 13.426$ (6) Å, $\beta = 101.4$ (2) Å, $Z = 4$, $D_c = 1.24$ g/cm³. X-ray data collection was performed with Trombay computer-controlled diffractometer equipped with Mo target tube ($\gamma = 0.7107$ Å). The structure was solved by direct methods, which revealed the locations of all nonhydrogen atoms on the initial E map. Hydrogen atoms were kept fixed. There are two independent molecules in the asymmetric unit with same conformation.

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¹Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.