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ISOLATION OF EPOXYDECOMPOSTIN FROM LEPIDOSPARTUM SQUAMATUM GRAY AND ITS STRUCTURE REVISION

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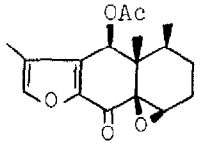
In the past few years several sesquiterpenes of the furanoeremophilane type have been isolated from members of the tribe Senecioneae of the family Compositae[1-5]. Because of a question about the classification of Lepidospartum squamatum Gray we decided to examine its constituents. The major compound isolated was epoxydecompostin[3] 1. Only trace amounts of related compounds could be detected. The content of epoxydecompostin in some samples was so high that it crystallized from a hexane extract of the dried plant. Various plant collections yielded 0.3-0.7% of 1.



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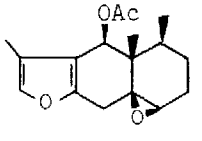

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All of the published data[3] on 1 were matched by our compound and comparison of the two samples by professor Bohlmann showed we had identical compounds. As part of our characterization we obtained ^{13}C and 300 MHz H nmr spectra which are summarized in the tables.

The proposed stereochemistry[3] of the epoxide ring in 1 is based upon the stereochemistry of 2. The angelyl ester of 2 was isolated by another group[5] who proposed the opposite stereochemistry of the epoxide ring. We can now clear up this uncertainty for 1 since we have carried out an X-ray structure determination on it.

A clear, white crystal of epoxydecompostin ($C_{17}H_{20}O_5$) measuring 0.3 mm x 0.3 mm x 0.5 mm was subjected to X-ray diffraction analysis and was found to belong to the unambiguous orthorhombic space group $P_{2_12_12_1}$ with $\underset{\sim}{a} = 15.797(3)$, $\underset{\sim}{b} = 12.048(2)$, $\underset{\sim}{c} = 8.170(1)$. A total of 1246 unique reflections with $2\theta \leq 114^\circ$ was measured on a fully automated four-circle diffractometer using monochromated CuK_α (1.5418Å) radiation. Periodically monitored standard reflections showed no decrease in intensity over the time of data collection. After Lorentz, polarization, and background corrections 1120 (90%) reflections were judged observed $F_o^2 > 3\sigma(F_o^2)$.

A multiple solution, weighted tangent formula approach[6] was used to assign phases to the 100 largest E's greater than 1.56. The resulting E map showed 20 atoms and a subsequent F map revealed the two remaining atoms. Full matrix least squares refinements using anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms smoothly converged to an unweighted crystallographic residual of 0.032[7]. All bond distances and angles agree with generally accepted values[8,11].

^{13}C NMR PARAMETERS[9]

Chemical Shift ppm	ORCW Multiplicity	Carbon Assignment
8.21	q	13
15.53	q	14, 15
15.76	q	14, 15
19.30	t	2, 3
20.75	q	17
24.82	t	2, 3
32.13	d	4
45.11	s	5
62.50	d	1, 6
65.39	s	10
69.33	d	1, 6
121.58	s	11
136.90	s	7
146.38	s	8
146.83	d	12
170.56	s	16
180.81	s	9

300 MHz NMR PARAMETERS[10]

		δ (TMS)	Coupling Analysis
H_1	X	3.37 equatorial	J_{AB} = -15.4
H_2	A	2.05 axial	J_{AC} = 11.2
	B	1.93 equatorial	J_{AE} = 6.0
H_3	C	1.80 axial	J_{AX} = 0.7
	E	1.47 equatorial	
H_4	D	1.62 equatorial	J_{BC} = 6.8
H_6		6.65	J_{BE} = 3.0
H_{12}		7.50 $J_{12,13}\sim 0.5$	J_{BX} = 4.5
H_{13}		1.97	
H_{14}	F	1.04	J_{CE} = -14.0
H_{15}		1.23	J_{CD} = 4.0
H_{17}		2.25	
			J_{DE} = 4.2
			J_{DF} = 7.1

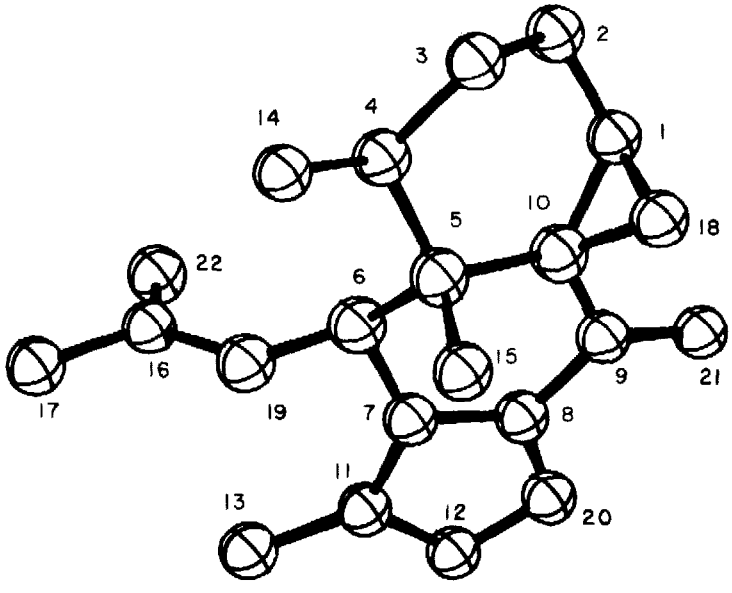

Figure. A computer generated view of epoxydecompostin

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9. ^{13}C spectra were run in $CDCl_3$ on a Varian CFT-20 spectrometer; chemical shifts are relative to TMS.

10. Nmr spectra were run on a Varian HR-300 spectrometer in $CDCl_3$. Coupling constants were determined with the aid of double resonance experiments.

11. Tables of fractional coordinates, bond distances, bond angles and observed and calculated structure factors are available as a Supplement to Publication. To obtain a copy contact the Photo Service, Iowa State University, Ames, Iowa 50011, requesting Supplement to Publication, B.L. Flamm, Tetrahedron Letters (1976) and submitting $.50 in the form of check, cash or money order. Give your name and complete address (including zip code) for mailing.

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