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A *C*-FORMYLATED AZULENE FROM *LACTARIUS DETERRIMUS*

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Key Word Index—*Lactarius deterrimus*; Agaricaceae; 1-formyl-4-methyl-7-isopropyl azulene (11,12-dihydro-lactaroviolin); D-mannitol; palmitic acid, stearic acid; ^{13}C NMR.

Abstract—1-Formyl-4-methyl-7-isopropyl azulene (11,12-dihydro-lactaroviolin) was characterized from *Lactarius deterrimus* together with other known compounds.

The fungus *Lactarius deterrimus* Groger has a wide distribution in the pine forests of Kashmir. It is edible and occurs in abundance from July to September. Its fruit body is pale peach coloured and becomes apricot coloured with a greyish green intensity on aging. On cutting, it yields saffron or orange coloured latex which fades in colour after an hour. There is no chemical work reported on this species although many investigations have been reported on the sister species [1–5]. In this communication we report the isolation and characterization of 1-formyl-4-methyl-7-isopropyl azulene (11,12-dihydro-lactaroviolin) (**1**) from the above species. Although **1** has been reported as an oxidation product of 1,4-dimethyl-7-isopropyl azulene [6], this to our knowledge is the first report of its isolation from a natural source. Most of the azulenes which have been isolated from natural sources are not found in the living plant but are formed as a result of enzymatic oxidation during the drying of the fruit bodies. In this study we have used very mild extraction and purification conditions and the cold hexane and methanol extracts both showed the presence of a purple coloured pigment which is also the colour of the fresh fungus, indicating that **1** may not be an artefact.

The ^1H NMR spectrum of **1** exhibited a doublet at $\delta 1.33$ ($J = 7$ Hz) for the protons of an isopropyl group and a methyl proton signal was present at $\delta 2.83$ as a sharp singlet. A C-8 proton signal was located at $\delta 9.56$ as a weakly coupled singlet and an aldehydic proton signal was located at $\delta 10.2$. The aromatic proton signals were found between $\delta 7.0$ and 7.5 in the form of a multiplet. Reduction of **1** under controlled conditions furnished an alcohol in which the signals of the CH_2OH protons appeared at $\delta 4.73$ with the disappearance of the signal for the aldehyde proton. In addition, C-8 proton signal was moved upfield and merged with the other aromatic signals.

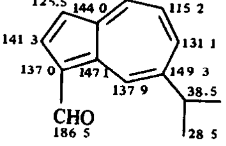
The structure of **1** was confirmed through its mass spectral fragmentation pattern and 90 MHz ^{13}C NMR spectrum (see **1**).

EXPERIMENTAL

The fruit bodies were collected from Tangmarg, Gulmarg forest of the Kashmir valley, and identified by the Botanical section of this Institute (Herbarium accession No. RRL MH-5). The dried material (275 g) was extracted with MeOH and the dark purple extract concd in a vacuum. A crude solid which separated out was crystallized from dilute EtOH and identified as D-mannitol [mmp (165.5°), acetate formation, co-TLC and MS]. The resinous mother liquor was chromatographed on Al_2O_3 (neutral) and eluted with petrol–C_6H_6, C_6H_6, EtOAc and MeOH in increasing proportions. Compound **1** was isolated from the early fractions while the later fractions gave a solid mixture of acids, two of which were identified as palmitic and stearic acids by MS and GLC (R_ts of methyl esters). **1** was a purple coloured solid, mp 59–60°, and was very sensitive to acids. UV/VIS λ_{max}^{MeOH} nm: 230, 314, 378, 390, visible 530, 575 (sh) and 630; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2930, 2900, 2785, 2710, 2396, 2300, 1650, 1490, 1425, 1400, 1280, 1200, 1020 and 950; MS *m/z* (rel. int.): 212 (100), 197, 182, 169, 154, 141, 128, 115, 83 and 63; ^1H NMR ($CDCl_3$): $\delta 1.33$ ($2 \times 3H$, *d*, $J = 7$ Hz, isopropyl methyls), 2.83 (3H, *s*, Me-6), 2.7–3.25 (1H, *m*, methine), 7.0–7.5 [3H, *m*, H-3, H-5, H-6 (aromatic)], 7.96 (1H, *d*, $J = 4$ Hz, H-2), 9.56 (1H, *s* (*br*), H-8) and 10.2 (1H, *s*, aldehydic H).

Reduction of **1** with $LiAlH_4$ in Et_2O furnished a semi-solid, **1a**. ^1H NMR ($CDCl_3$): $\delta 1.30$ ($2 \times 3H$, $J = 7$ Hz, isopropyl), 2.86 (3H, *s*, Me-6), 2.60–3.0 (1H, *m*, methine), 4.73 (2H, *s*, $C\underline{H}_2OH$), 6.70–7.50 (4H, *m*, Ar-H).

Acknowledgement—We are grateful to the Instrumentation Division for running the spectra.



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AN ACETYLENIC EPOXIDE AND A FERULATE FROM *COREOPSIS LONGULA*

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Key Word Index—*Coreopsis longula*; Compositae; acetylenes; hepta-decatetraendiyne derivative; ferulic acid ester.

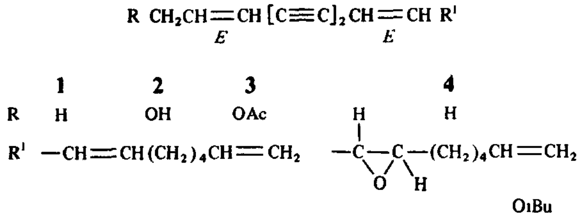
Abstract—The aerial parts of *Coreopsis longula* gave, in addition to known compounds, a new acetylenic epoxide, hepta-deca-1,9*E*,15*E*-trien-11,13-diyn-7,8-epoxide, while the roots afforded a new ferulate, coniferyl ferulate.

Many species from the large genus *Coreopsis* (tribe Heliantheae) have been studied chemically. In addition to acetylenic compounds, flavonoids and phenyl propane derivatives [1] may be characteristic of the genus. We have now studied *Coreopsis longula* Blake from Peru. The aerial parts of this plant gave the epoxide **5** [1], the acetylenic compounds **1–3** [1] and the new epoxide **4**. The molecular formula of **4**, $C_{17}H_{20}O$, was deduced from the chemical ionization mass spectrum while the UV spectrum indicated the presence of an endiyne [1]. The ^{1}H NMR spectrum showed the presence of a vinyl end group and a propenyl end group. As all the signals were assigned by spin decoupling, the position and the configuration of the double bonds and the epoxide were determined. Thus **4** was the epoxide of **1**.

The roots also contained **1**, **4** and **5** as well as **6** [1] and the ferulate **7**, the structure of which followed from the ^{1}H NMR spectra of **7** and its acetate **8**.

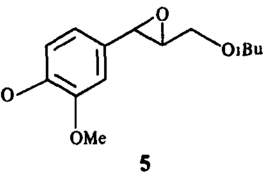
EXPERIMENTAL

The air-dried plant material (voucher RMK 9189, collected in January 1983 in Peru) was worked-up in the usual fashion [2]. The extract of the aerial parts (300 g) was separated by CC and gave the following fractions: 1 (petrol), 2 (Et_2O–petrol, 1:9), 3 (Et_2O–petrol, 1:3) and 4 (Et_2O and Et_2O–MeOH, 8:1). TLC (petrol) of fraction 1 gave 50 mg **1** and TLC (Et_2O–petrol, 1:5) of fraction 2 afforded 2 mg **4** (R_f 0.70), 2 mg **3** and 3 mg **5**. TLC of fraction 3 (Et_2O–petrol, 1:1) gave 2 mg **2**, while fraction 4 gave nothing of interest. CC of the extract of the roots (100 g) gave the following fractions: 1 (petrol and Et_2O–petrol, 1:20), 2 (Et_2O–petrol, 1:3) and 3 (Et_2O–petrol, 1:1 and Et_2O). TLC of fraction 1 (petrol) gave 2 mg **1** and 2 mg **4**. TLC (Et_2O–petrol,



$$\mathrm{R\ CH_2}\underset{E}{\mathrm{CH{=}CH}}[\mathrm{C{\equiv}C}]_2\underset{E}{\mathrm{CH{=}CH}}\ \mathrm{R'}$$

	1	2	3	4
R	H	OH	OAc	H
R'	$-\mathrm{CH{=}CH(CH_2)_4CH{=}CH_2}$			$-\overset{\mathrm{H}}{\mathrm{C}}\underset{\mathrm{O}}{-}\underset{\mathrm{H}}{\mathrm{C}}-\mathrm{(CH_2)_4CH{=}CH_2}$



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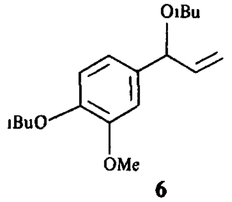

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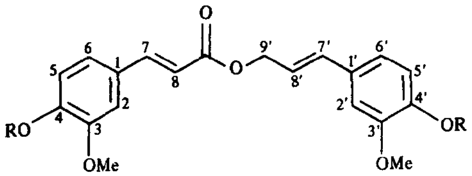

7 R = H
8 R = Ac