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THE STRUCTURE OF NEW SESQUITERPENES FROM BASIDIOMYCETES

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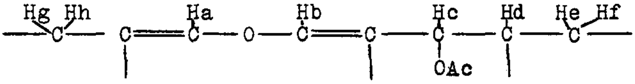
Fomannosin[1)] **7** is a metabolite of the wood-rotting fungus, <u>Fomes</u> <u>annosus</u> Karst, which causes decay of the living wood. This substance was reported to have a phytotoxic activity toward seedlings of <u>Pinus</u> <u>tadea</u>.[2)] In the course of an investigation of biosynthesis of the fungal isoprenoids produced by Basidiomycetes, we have isolated two new furanoid sesquiterpenes along with fomannosin **7**, from <u>Fomitopsis</u> <u>insularis</u> which was nonpathogenic and commonly found on pine tree. We assign structure **1** and **3** to these substances from their physicochemical properties.

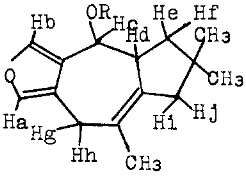
The compound **1**, $C_{15}H_{20}O_2$ (M^+, 232) had $[\alpha]_D$ +69.5°, λ_{max} 215 nm (ε, 5100): ν_{max} 3610, 3490, 876 cm^{-1}. The nmr spectrum of **1** shows the signals at δ 0.88, 1.13, 1.72 (three methyl groups), 4.23 (1H, d, J=11 Hz, a methine proton on a carbon bearing a hydroxyl group), 3.33, 2.88 (ABq, J=16 Hz, an allylic methylene) and 7.04, 7.72. The presence of the β,β-disubstituted furan ring was indicated by nmr, ir (876 cm^{-1}) uv and mass fragmentation (<u>m/e</u> 81).

Double resonance experiments on the acetate **2** indicate that the following proton arrangement must be involved in **2**, coupling constants are shown as follows respectively: Jab=1.8 Hz, Jbc=1.0 Hz, Jcd=10.5 Hz, Jde=7.5 Jdf=9 Hz, Jef 13 Hz, Jga=1.0 Hz, Jah $\simeq$ 0, and Jgh=16 Hz.

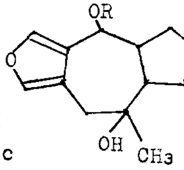


$$-\overset{H_g\ H_h}{C}-\quad \underset{|}{C}=\overset{H_a}{C}-O-\overset{H_b}{C}=\underset{|}{C}-\underset{OAc}{\overset{H_c}{C}}-\underset{|}{\overset{H_d}{C}}-\overset{H_e\ H_f}{C}-$$

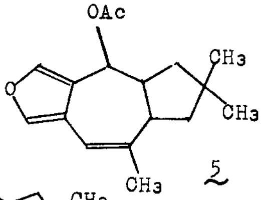
The compound **3**, $C_{15}H_{22}O_3$ (M^+, 250), nmr (δ) 1.02 (s, 6H), 1.18 (s, 3H), 2.87, 2.65 (ABq, J=16 Hz), 4.60 (d, J=5 Hz), 5.25 (br.s, 2H), 7.10, 7.22 (1H each) gives a crystalline monoacetate **4**, $C_{17}H_{24}O_4$ (M^+, 292), m.p. 125°, nmr (δ) 1.06, 1.08, 1.19 (each 3H), 2.08 (s, 3H) 2.48, 2.81 (ABq, J=15 Hz), 5.79 (d, J=8 Hz), 7.09, 7.16. The presence of furan ring in 3 was supported by readily formation of the Diels-Alder adduct with diethyl acetylenedicarboxylate to give compound 6. Treatment of the acetate 4 with phosphorus oxychloride in pyridine afforded a dehydration product, 5, $C_{17}H_{22}O_3$ (M^+, 272): λmax 238 nm (ε, 6280). In the nmr spectrum of 5, one of the tertiary methyl signal in 4 (1.19) shifts to 1.88 and a new olefinic proton signal appeared at δ 6.00 (br. s, 1H). These data show that the structure of 3 has the same skeleton as 1.



1;R=H
2;R=Ac



3;R=H
4;R=Ac



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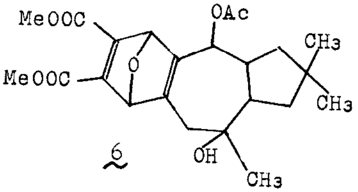

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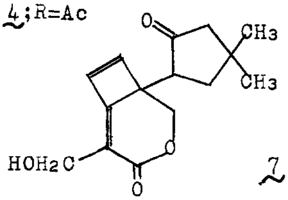

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From the data mentioned above, the two compounds must have structures 1 and 3 respectively. It is considered that the compounds have close biogenetical relationship to marasmic acid.[3] Co-occurrence of 1 and fomannosin 7 suggests the biogenesis of both compounds.

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