CHEMISTRY LETTERS, pp. 1837 - 1838, 1984.

ON THE STRUCTURES OF PISIFERIN AND ISOPISIFERIN

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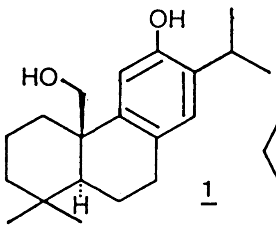
The structure of pisiferin has been revised, and the double bond isomer, named isopisiferin, has been found in the seed of *Chamaecyparis pisifera*.

"Pisiferin" is a diterpene isolated from the leaves of *Chamaecyparis pisifera* (Cupressaceae) together with some C-20 oxygenated abietane-type diterpenes including pisiferol(1), and the chemical structure 2 has been proposed by Yatagai and Takahashi1) on the basis of spectral analyses, some chemical transformations and a correlation with 1.



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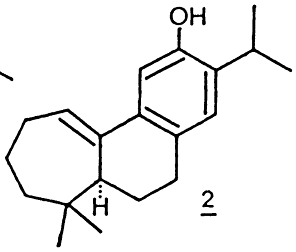

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Recently, we investigated the terpenic constituents in the seed of *Ch. pisifera*, and obtained "pisiferin" along with a number of related diterpenes, some of which were the same as in the leaves. However, "pisiferin" obtained by repeated chromatography of the seed extract on silica gel and on LiChroprep RP-8 was found to be a mixture of two compounds. The mixture, after acetylation, was separated by chromatography on 10% $AgNO_3$-impregnated silica gel to give two acetates in a ratio of 8:3. On treatment with LAH, the acetates gave original compounds, respectively.

We now wish to leave the name, pisiferin, for the major component and give a name, isopisiferin, to the minor one, and describe their structural determination.

Pisiferin(3), $C_{20}H_{28}O$, a colorless oil, $[\alpha]_D^{25}$ -87.4 °(c 1.75, $CHCl_3$), shows the presence of a phenolic hydroxyl group by a positive iron(III) chloride-pyridine test, the IR absorption bands at 3400,1610,1500, and 1163 cm^{-1}(neat) and the UV absorption maximum at 281 nm(ε 2614). The ^1H NMR spectrum(see Table 1) reveals the presence of a 2,4,5-trialkylated phenolic ring, an isopropyl group attached to an aromatic ring, two tertiary methyl groups and a trisubstituted double bond. Besides, the signals at δ 3.22(2H,br s) and 2.78(2H,m) indicate the presence of two benzylic methylene groups, disproving the structure 2.

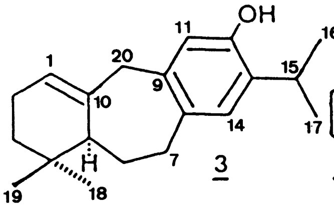
Isopisiferin(4), $C_{20}H_{28}O$, colorless prisms, mp 87-90 °C, $[\alpha]_D^{25}$ -193.1 °(c 2.56, $CHCl_3$) gave an acetate, mp 145-146 °C, and also indicates the presence of a phenolic hydroxyl group by a positive iron(III) chloride-pyridine test and the IR absorption bands at 3350,1610,1500, and 1160 cm^{-1}(KBr), and the presence of a

Table 1. ^{1}H NMR spectra(100 MHz,$CDCl_3$) of pisiferin(3), isopisiferin(4) and 5

	H-1	H-6	H-7	H-11	H-14	H-15	H-16, 17	H-18, 19	H-20
3	5.36 t, J=4Hz		2.78 m	6.46 s	6.84 s	3.12 sept,J=7Hz	1.21,1.21 each d,J=7Hz	0.90,0.87 each s	3.22 br s,$W_{\frac{1}{2}}$=4Hz
4	2.20 m		2.62 m	6.43 s	6.77 s	3.13 sept,J=7Hz	1.20,1.23 each d,J=7Hz	0.93,0.68 each s	6.17 br s,$W_{\frac{1}{2}}$=4Hz
5	2.04 br t, J=7Hz	2.38 m	2.87 m	6.40 s	6.81 s	3.12 sept,J=7Hz	1.22,1.22 each d,J=7Hz	0.98,0.98 each s	3.23 br s,$W_{\frac{1}{2}}$=4Hz

trialkylated phenolic ring, an isopropyl group attached to the aromatic ring, two tertiary methyl, one benzylic methylene groups, and a trisubstituted double bond by the ^{1}H NMR spectrum(see Table 1). The trisubstituted double bond is indicated to be conjugated with the phenolic ring by the absorption maxima at 262(ε 11083),299 (3307), and 310 nm(shoulder) in the UV spectrum and the olefinic proton signal at δ 6.17(1H,br s) in the ^{1}H NMR spectrum. Hydrogenation of 3 and 4 over Pd-C gave an identical dihydro compound as an inseparable mixture of epimers at C-10, hence 4 is a double bond isomer of 3.

Detailed reexamination of the reaction of 1 with thionyl chloride in benzene at room temperature for 3 h revealed the formation of 3, 4, and 5,[2)] the last of which was an optically inactive colorless oil, having a tetrasubstituted double bond. These results led us to the conclusion that 3, 4, and 5 had the same carbon skeleton, the B ring being a seven-membered ring.



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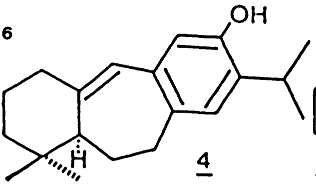

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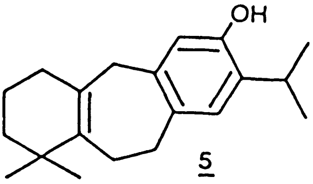

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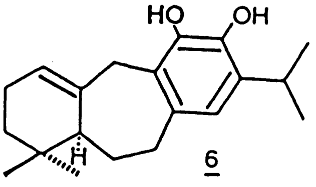

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Recently barbatusol, isolated from Coleus barbatus(Labiatae) by Kelecom, has been shown to be represented by 6.[3)] In order to establish the structure 3 for pisiferin, conversion of pisiferin into barbatusol was successfully carried out by treatment of pisiferin with benzoyl peroxide in chloroform at 60 °C for 4 h, followed by LAH. The product obtained was identical with barbatusol in all respects (MS, UV, IR, ^{1}H and ^{13}C NMR, and $[\alpha]_D$). Thus, the structures of pisiferin and isopisiferin were determined as 3 and 4, respectively.

We wish to thank Dr. A. Kelecom, Marine Natural Products Laboratory, Dept. of General Biology, Universidade Federal Fluminense, for sending us copies of the IR, ^{1}H NMR and MS spectra of barbatusol.

References

1) M. Yatagai and T. Takahashi, Phytochemistry, 19, 1149 (1980).

2) 5: $C_{20}H_{28}O$, UV(EtOH): 282 nm(ε 2393), IR(neat): 3400,1610,1500, and 1160 cm^{-1}, ^{1}H NMR(Table 1). The ^{13}C NMR spectrum shows the presence of two sp_2 carbon atoms bearing no proton in addition to four ones of the phenolic ring.

3) A. Kelecom, Tetrahedron, 39, 3603 (1983).

(Received August 9, 1984)