

extract, and Dr. Emsley and Mrs. J. Street, University of Southampton, England for the NMR spectra.

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DITERPENES OF THE FERRUGINOL TYPE FROM *CHAMAECYPARIS PISIFERA*

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Key Word Index—*Chamaecyparis pisifera*; Cupressaceae; ferruginol type; methyl pisiferate; pisiferol.

In a previous paper [1], we reported the isolation of a new phenolic diterpene acid, pisiferic acid (1), from the leaves of *Chamaecyparis pisifera* (Cupressaceae). Further examination of the leaves has now led to the isolation of a phenolic diterpene alcohol (2), named pisiferol, and methyl pisiferate (3) [1].

On the basis of the spectral data (IR, NMR, UV spectra), pisiferol (2) was identified as 12-hydroxyabieta-8,11,13-trien-20-ol which had been synthesized previously by us from pisiferic acid (1) by treatment with sodium dihydro-bis(2-methoxyethoxy)aluminate [1]. It was for the first time that pisiferol (2) and methyl pisiferate (3) were isolated from natural sources.

Although the presence of ferruginol (4) [2] was estimated by co-chromatography (TLC, Si gel) of the

methanol extract with an authentic sample, ferruginol could not be isolated because of its small content in the leaves.

EXPERIMENTAL

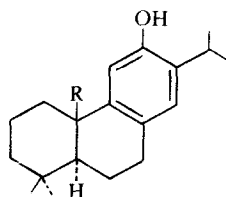
Pisiferol (2). The fresh leaves of *Chamaecyparis pisifera* (200 g), collected in Tokyo in January 1978, were extracted with MeOH for 1 week. Evapn yielded an extract (5 g), which was partitioned between Et₂O and H₂O. The Et₂O-soluble fraction (2 g) was chromatographed on Si gel (Merck, Kieselgel 60, 70–230 mesh 80 g). Elution with C₆H₆ followed by Et₂O yielded an enriched pisiferol fraction (250 mg), and a portion (150 mg) of the enriched fraction was subjected to PLC on Si gel (Merck, Kieselgel GF₂₅₄₊₃₆₆, eluent CHCl₃–HOAc, 20:1) to give crude pisiferol. The crude pisiferol was recrystallized from C₆H₆–Et₂O to give pure needles of pisiferol (2) (95 mg).

Methyl pisiferate (3). A portion (1 g) of the above MeOH extract was chromatographed on Si gel. Elution with *n*-hexane followed by C₆H₆ yielded a crude phenolic diterpene alcohol fraction (140 mg). The fraction was rechromatographed on Si gel to give a pure compound (82 mg) which was identical (TLC, IR, NMR spectra) with the authentic sample of methyl pisiferate (3).

Chromatography of the C₆H₆ extract of the leaves on Si gel using C₆H₆ as eluent also gave methyl pisiferate (3).

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- 1 R = CO₂H
- 2 R = CH₂OH
- 3 R = CO₂Me
- 4 R = CH₃