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PINGUISANE-TYPE SESQUITERPENES FROM *PTILIDIUM PULCHERRIMUM*

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Key Word Index—*Ptilidium pulcherrimum*; Ptilidiaceae; Jungermanniales; Hepaticae; pinguisane-type sesquiterpenes; pinguisanin; pinguisanolide; pinguisenal; isopinguisanolide; chemosystematics.

Abstract—Three sesquiterpenes, pinguisanin, pinguisanolide and pinguisenal, have been isolated from the liverwort, *Ptilidium pulcherrimum*. These pinguisane-type sesquiterpenes are significant chemosystematic markers of Ptilidiaceae. *Ptilidium* species are chemically close to some *Porella* and *Lejeunea* species.

INTRODUCTION

Most liverworts belonging to Jungermanniales produce mono-, sesqui- and/or diterpenoids as major components. Recently, we reported the distribution of terpenoids and lipophilic aromatic compounds in more than 100 species of the liverworts [1–7] and it is apparent that endogenous biochemical characters are unambiguously significant in the taxonomic investigation of bryophytes.

Ptilidium species are rather primitive liverworts in Jungermanniales [8]. Krutov *et al.* [9] reported that *Ptilidium ciliare* (L.) Nees. elaborated a furanosesquiterpene, deoxopinguisone (**5**). This unique furanosesquiterpene and its derivatives were also found in some *Lejeunea* [6], *Trichocoleopsis* [10] and *Porella* species [11–13]. The present paper summarizes the results obtained from a European sample of *P. pulcherrimum* which proved to be a rich source of pinguisane-type sesquiterpenes.

RESULTS AND DISCUSSION

Air-dried ground material was extracted with Et_2O and the crude green oil was directly chromatographed on Si gel to afford three pinguisane-type sesquiterpenes, pinguisanin (**1**) and pinguisanolide (**2**) as the major components, and pinguisenal (**3**) as the minor one. In addition to the above pinguisane-type sesquiterpenes, phytosterol mixtures (campesterol, stigmasterol and sitosterol), which are distributed in all the liverworts so far examined, were obtained. A sesquiterpene hydrocarbon, β-caryophyllene, and isopinguisanolide (**4**) have been detected by GC/MS.

The spectral properties and chromatographic behaviour of pinguisane-type sesquiterpenes **1–3** were identical to those of the authentic samples previously isolated from European *Porella platyphylla* (L.) Lindb. and a Japanese sample of *Trocholejeunea sandvicensis* (Gott.) Mitz. [6, 13]. The mass spectrum of isopinguisanolide was the same as that of pinguisanolide (**2**), although the retention times of the two compounds were different. Thus, it is suggested that the isopinguisanolide (**4**) may be the C-6 epimer of **2**.

Deoxopinguisone (**5**) found in *P. ciliare* [9] and norpinguisane-type sesquiterpenes in some *Porella* species [10–12] have not been detected in *P. pulcherrimum*. It is suggested that pinguisane-type sesquiterpenes may be significant chemosystematic markers in Ptilidiaceae. Furthermore, it is interesting from the standpoint of the evolution of Jungermanniales that the same pinguisane-type sesquiterpenes **1–3** have been found as the major components in different members of the same genera

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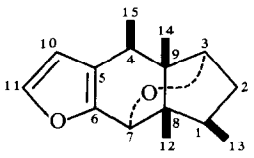

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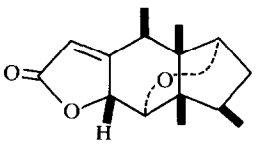

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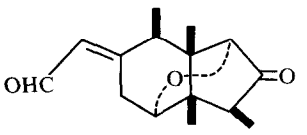

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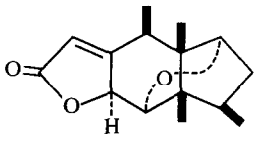

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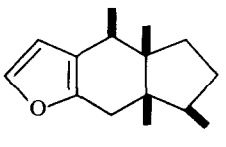

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within the families Porellaceae and Lejeuneaceae. On the basis of the above chemical results, it is clear that some species of *Porella*, *Lejeunea* and *Ptilidium* are biochemically closely related.

EXPERIMENTAL

IR, ^{1}H NMR, GC/MS and $[\alpha]_D$ were measured as reported in previous papers [1, 13]. TLC and GC were carried out in the same manner as described earlier [13].

Plant material. Ptilidium pulcherrimum (Web.) Hampe, collected in Jungraukorp, Haut-Rhin, France on 2 September 1979 and identified by C.S., is deposited in the Herbarium, Institute of Pharmacognosy, Tokushima Bunri University.

Extraction and isolation. P. pulcherrimum was air-dried for 5 days and the ground material (24.50 g) was extracted with Et_2O for 10 days. The crude extract (1.085 g) was directly chromatographed on Si gel using a *n*-hexane–EtOAc gradient. The first fraction eluted with *n*-hexane gave sesquiterpene mixtures (9 mg) in which β-caryophyllene was detected by GC/MS. The second fraction (*n*-hexane–EtOAc, 19:1) contained carotenoids (7 mg). The third fraction (9:1) gave triglycerides (320 mg). The fourth fraction (7:3) gave mixtures of furanosesquiterpenes (256 mg) which showed three peaks in GC (R_t = 9.7, R_t = 11.4, R_t = 11.8; 17:19:1). The mass spectrum of the component (R_t = 11.4), measured by GC/MS, was the same as that of the component (R_t = 11.8) except for the small difference on the relative intensities of each fragment ion. The mixtures were rechromatographed on Si gel using C_6H_6 to afford pinguisanin (**1**) (98 mg) and pinguisanolide (R_t = 11.4) (**2**) (140 mg) whose spectral data and chromatographic behavior were identical to those of the authentic samples [13]. The compound (R_t = 11.8) named isopinguisanolide was not isolated; however, its structure was tentatively assigned as the C-6 epimer (**4**) of pinguisanolide (**2**) by the mass spectrum. Compound (**4**): GC/MS *m/z* (rel. int.): 248 (M^+, 1), 194 (8), 192 (10), 137 (14), 127 (20), 109 (80), 108 (10), 97 (100), 96 (20), 41 (15). The fifth fraction (4:1) (180 mg) was rechromatographed on Si gel using a C_6H_6–EtOAc gradient to afford pinguisenal (**3**) (13 mg) [6] and phytosterol mixtures (90 mg) (campesterol: stigmasterol: sitosterol, 2:3:1 in GC). The sixth fraction (3:2) gave fatty acids (38 mg). The seventh (1:1), eighth (1:2) and ninth fractions (EtOAc, 100%) were not identified because of lack of samples.

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