The minor components (Table 1) were identified by employing gas chromatography using DEGS and PEG 6000 without further separation: peaks 2, 3, 5 and 9 were respectively identified as methyl undecanoate, laurate, myristate and stearate, and peaks 1, 4 and 6 as methyl decanoate, tridecanoate and pentadecanoate by applying linear relationship between logarithumus of the retention times and carbon atom numbers in the methyl esters of a fatty acid homologs. The remained peak 8 was attributed to methyl oleate, because it agreed with that of an authentic specimen, and also because it disappeared and the peak of methyl palmitate was enhanced after catalytic hydrogenation.

The relative concentrations of the components are shown in Table 1. In order to show that the methyl esters were not artifacts of the methanol extraction, another experiment was carried out using ethyl acetate as an extraction solvent; the methyl esters were again detected.

EXPERIMENTAL

The PMR spectrum was taken on a 60 MHz spectrometer in $CDCl_3$. The gas chromatography was carried out with a flame ionization apparatus in connecting with a separation column (3 mm × 3 m) which was packed with DEGS (10%) or PEG 6000 (3%) on Diasolid L(60–80 mesh). Oven temperature was 180° and nitrogen gas was used as a carrier.

Material and its Extraction

P. fabbroniana was collected in the suburbs of Hiroshima City, dried in the shade for a few days, and then digested with methanol at room temperature. The methanol solution was concentrated to a small volume, and then steam distilled. The distillate was extracted with $CHCl_3$ to give an oily substance; $[\alpha]_D^{25}$ O, n_D^{25} 1·4374, d_4^{25} 0·8758.

Isolation of the Major Constituent

The oily substance was chromatographed over silica gel-packed column (1·7 × 42 cm) in C_6H_6–$CHCl_3$ (1:1). 3 ml Fractions were collected and from the middle fractions the major constituent was obtained in the homogeneous state regarding gas chromatography (DEGS and PEG 6000) and TLC(R_f 0·52, C_6H_6–$CHCl_3$, 1:1).

Hydrogenation of the Steam-volatile Substance

The oil (0·30 g) was hydrogenated over Adams catalyst (0·03 g) in HOAc (6 ml). After 2 hr the absorption of H_2 ceased.

Acknowledgement—The authors are indebted to Dr. Tarô Seki, Department of Botany, Hiroshima University, for identifying the plant material.

Phytochemistry, 1971, Vol. 10, pp. 432 to 433. Pergamon Press. Printed in England.

MUSCI

21-HOPENE AND SOME OTHER CONSTITUENTS OF *PSEUDOSCLEROPODIUM PURUM**

A. MARSILI, I. MORELLI and A. M. IORI

Istituti di Chimica Farmaceutica e di Chimica Organica dell'Università di Pisa, 56100 Pisa, Italy

(*Received* 28 *May* 1970, *in revised form* 10 *July* 1970)

Abstract—21-Hopene, 22(29)-hopene and ursolic acid were isolated from a moss. Cyclolaudenol, 31-norcyclolaudenol, three sterols and a number of aliphatic hydrocarbons and fatty acids were also detected.

* Triterpenes from mosses, III. For parts I and II see: A. MARSILI and I. MORELLI, *Phytochem.* **7**, 1705 (1968); A. MARSILI and I. MORELLI, *Phytochem.* **9**, 651 (1970).

ALTHOUGH 21-hopene (A'-neogammacer-21-ene) is well known,[1] it has not previously been found in a natural source. Now, this triterpene has been isolated from the moss *Pseudoscleropodium purum* Fleisch. Identification was made by NMR spectrometry, direct comparison with a synthetic sample,[1] and transformation into the known hopane-21,22-diol,[2] bisnoradiantone,[3] and isobisnoradiantone.[3]

Other triterpenes are also present in *Pseudoscleropodium*; namely, 22(29)-hopene, ursolic acid,[4] cyclolaudenol,[5] and 31-norcyclolaudenol;[5] sterols (mainly campesterol, stigmasterol and β-sitosterol) and normal alkanes from C_{23} to C_{32}. In the saponified extract, fatty acids from C_{12} to C_{24} were detected.

We studied two different samples of the moss. The results show that the ratio between 21-hopene and 22(29)-hopene depends upon time of collection of the plant: it was 23:77 in February and 71:29 in October, the total amount of the two triterpenes being almost the same. This suggests that 21-hopene is formed by rearrangement of 22(29)-hopene in the plant, and not by a reaction involving concomitant formation of the two olefines from a common cationoid precursor.

EXPERIMENTAL

For more complete experimental details about extraction and fractionation procedures, see parts I and II. Waxes and ursolic acid were obtained by concentration of the extract; hydrocarbons were separated from alcohols by chromatography over alumina; aliphatic from triterpenoid hydrocarbons, and 21-hopene from 22(29)-hopene were separated by chromatography over silica gel impregnated with $AgNO_3$ (eluants: light petroleum and benzene). The components of the alcoholic fractions were identified as trimethylsilyl ethers by GLC, and by TLC (silica gel Merck F 254; eluant for free alcohols: $CHCl_3$–MeOH 99·5:0·5; for benzoates: cyclohexane–AcOEt 99:1). Comparison with authentic samples was always made.

Percentages of compounds with respect to the dried plant: waxes, 0·25; 21-hopene + 22(29)-hopene, 0·016; aliphatic hydrocarbons, 0·05; ursolic acid, 0·07; cyclolaudenol, 0·008; 31-norcyclolaudenol, 0·006; campesterol, 0·015; stigmasterol, 0·01; β-sitosterol, 0·015; fatty acids, 0·95. Relative amounts of aliphatic hydrocarbons (per cent, GLC): C_{23}, 0·5; C_{24}, 0·2; C_{25}, 0·5; C_{26}, 0·2; C_{27}, 5·7; C_{28}, 13·9; C_{29}, 16·8; C_{30}, 13·0; C_{31}, 46·6; C_{32}, 2·6. Relative amounts of fatty acids (per cent, GLC of methyl esters): lauric, 1·4; tridecanoic, 0·9; myristic, 1·8; pentadecanoic, 1·2; pentadecenoic, 0·9; palmitic, 33·5; palmitoleic, 1·3; hexadecadienoic, 2·8; heptadecanoic, 1·1; stearic, 3·6; oleic, 10·4; linoleic, 19·5; linolenic + arachidic, 4·4; gadoleic, 0·8; monocosanoic, 2·6; monocosenoic, 1·8; behenic, 5·9; tricosanoic, 1·0; lignoceric, 4·7.

Acknowledgements—We thank Professor U. Tosco (Torino) for the identification of the plant. This work was supported by a grant from the Consiglio Nazionale delle Ricerche (C.N.R.).

[1] (a) I. MORELLI and A. MARSILI, *J. Org. Chem.* **35,** 567 (1970); (b) R. E. CORBETT and R. A. J. SMITH, *J. Chem. Soc.* (C) 1622 (1967).

[2] W. J. DUNSTAN, H. FAZAKERLEY, T. G. HALSALL and E. R. H. JONES, *Croat. Chem. Acta* **29,** 173 (1957).

[3] G. BERTI, F. BOTTARI, A. MARSILI, J. M. LEHN, P. WITZ and G. OURISSON, *Tetrahedron Letters* 1283 (1963).

[4] Ursolic acid was also found in other mosses (Part II and yet unpublished work). However, the possibility that it derives from the humus in which these mosses grow cannot be rigorously excluded.

[5] Minor amounts of other cyclolanostanic triterpenes may be present in the plant, in addition to these compounds, as found in a fern [See: G. BERTI, F. BOTTARI, B. MACCHIA, A. MARSILI, G. OURISSON and H. PIOTROWSKA, *Bull. Soc. Chim. Fr.* 2359 (1964); E. L. GHISALBERTI, N. J. DE SOUZA, H. H. REES, L. J. GOAD and T. W. GOODWIN, *J. Chem. Soc.* (D) 1401 (1969)]. Indeed, other peaks were present in the GL chromatograms of the alcoholic fraction. It was not however possible to identify these other materials unambiguously.