La spectrométrie de masse montre aussi que l'ergostérol et le fungistérol sont accompagnés des pics de très faibles intensité à *m/e* 394 ($C_{28}H_{42}O$) et à *m/e* 398 ($C_{28}H_{46}O$), pouvant correspondre à leurs dérivés déshydrogénés.

PARTIE EXPERIMENTALE

Cultures. Lenzites trabea a été cultivé pendant 3 mois selon une technique déjà décrite.[1] A partir de ces cultures âgées d'un mois on a adapté la souche au milieu agité,[17] pendant 15 jours puis ensemencé dans un fermenteur "Biolafitte". Cette culture agitée a été poursuivie 15 jours à 30°.

Isolement des produits bruts. Le mycelium récupéré par centrifugation, lavé à l'eau et seché est extrait à l'aide d'un appareil Soxhlet, d'abord par l'éther de petrole pendant 20 hr (700 mg) puis par l'éther éthylique pendant 5 jours. On obtient ainsi 4,5 g de produit brut, que l'on cristallise dans le mélange isopropanol–éther–acétone. Les cristaux obtenus (800 mg) ont été chromatographiés sur une colonne de 50 g d'acide silicique impregné de CO_3Na_2 (50 g d'acide silicique sont homogeneisés dans 100 ml d'une solution 0,01 M de CO_3Na_2; on laisse sécher une nuit à la température du laboratoire et on l'active 30 min à 100° avant utilisation). Nous avons élué avec du benzène contenant des pourcentages croissants d'acétone (0, 15, 30 et 40%). Les premières fractions contiennent de petites quantités d'alcools triterpéniques; les fractions suivantes, de l'acide éburicoïque et des mélanges variables des acides éburicoïque et traméténolique.

Les fractions contenant les alcools triterpéniques ont été réunies et chromatographiées sur plaque préparative d'acide silicique (solvent, benzène–acétone 85:15); on isole ainsi une zone principale de R_f 0,56 qui contient comme produit majeur le méthylène-24 lanostérol. Les eaux mères de cristallisation ont été amenées à sec puis extraites par le benzène à 60°. La partie insoluble (700 mg) représente les dihydroxyacides: OH-15α traméténolique et sulfurénique. 1,4 g de la partie soluble dans le benzène ont été chromatographiés sur une colonne de 75 g d'acide silicique mélangé avec 25 g de celite. On développe avec de l'éther de pétrole contenant des pourcentages croissants d'éther éthylique (0, 2, 5, 10, 15, 20, 30 et 40%). Nous avons ainsi obtenu l'ergostérol, le fungistérol et les monohydroxyacides: éburicoïque et traméténolique.

Remerciements—Nous remercions M. le Professeur E. Lederer pour l'intérêt qu'il a porté à ce travail.

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Phytochemistry, 1971, Vol. 10, pp. 430 to 432. Pergamon Press. Printed in England.

BRYOPHYTA

HEPATICAE

FATTY ACID ESTERS IN THE VOLATILE OIL FROM THE LIVERWORT, *PELLIA FABBRONIANA**

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(*Received* 14 *May* 1970, *in revised form* 15 *July* 1970)

Abstract—Methyl decanoate, undecanoate, laurate, tridecanoate, myristate, pentadecanoate, palmitate, oleate and stearate were isolated as steam-volatile components from this liverwort. Total amounts of these methyl esters accounted for 75·3 per cent of the steam-volatile substances and methyl palmitate (60%) was the major constituent.

INTRODUCTION

DURING the last few years the following sesquiterpenes and related compounds have been detected in the essential oils of some liverworts: 1,4-dimethyl- and 4-methyl-1-methoxy-

* Chemical constituents from Hepaticae, Part V: Part IV, A. MATSUO and S. HAYASHI, *Tetrahedron Letters* 1289 (1970).

carbonyl-azulene, 3,7-dimethyl-5-methoxycarbonylindene,[1-3] (-)-longifolene, (-)-longiborneol,[4] drimenol,[5] pinguisone,[6] chiloscyphone[7,8] bazzanene,[9] and bazzanenol.[10]

We now report the isolation of a series of methyl esters of fatty acids from C_{10} to C_{18} as steam-distilled substances of *Pellia fabbroniana* Raddi (in Japanese Mizuzenigoke), a thalloidal liverwort belonged to the Metzgeriales of Hepaticae.

RESULTS

Air-dried plants were extracted with methanol, and then the extract was distilled with steam to obtain a pale yellow oily substance in yield of 0·13 per cent of the dried plants. The yield is only one-tenth of that obtained from *Chiloscyphus polyanthus* (1·06%) and *Bazzania pompeana* (1·20%); this low yield is attributed to the fact that oil bodies (4–6 × 4–5 μ, 10–20 pieces in a cell) are poor in *P. fabbroniana* compared with those in the two leafy liverworts.

The steam-volatile substance exhibited a gas chromatogram showing one major and several minor peaks. The chief component (peak 7) isolated by elution chromatography over silica gel exhibited absorption bands due to an ester bonding at ν_{max} 1743, 1245, 1165 and 1032 cm^{-1} and proton signals at δ_{ppm} 0·88 (3H, t, J = 6·5 Hz, primary methyl), 1·25 (26H, s, —CH_2—), 2·31(2H, t, J = 7·5 Hz, —CO—CH_2—) and 3·63(3H, s, —$COOCH_3$). The spectral evidence indicates this component to be methyl ester of a saturated fatty acid. The high resolution mass spectrum had a molecular peak at *m/e* 270·256 corresponding to $C_{17}H_{34}O_2$ (calc. *m/e* 270·256), and the low mass spectrum showed several fragment ions characteristic for a methyl ester: *m/e* 74(base peak, $[CH_2{=}C(OH){-}OCH_3]^+$), *m/e* 59(13·4%, $[COOCH_3]^+$), *m/e* 87(59·9%, $[CH_2CH_2COOCH_3]^+$) and *m/e* 239 (5·4%, $[C_{15}H_{31}CO]^+$). Thus, the chief component is methyl palmitate.

TABLE 1. CHEMICAL CONSTITUENTS OF VOLATILE OIL FROM *P. fabbroniana*

Peak No. of GLC	Components	(%)*
1	methyl decanoate	0·3
2	methyl undecanoate	2·4
3	methyl laurate	0·7
4	methyl tridecanoate	3·8
5	methyl myristate	1·3
6	methyl pentadecanoate	0·8
7	methyl palmitate	60·0
8	methyl oleate	4·0
9	methyl stearate	2·0

* The ratio of the chemical constituents were calculated on the basis of the relative peak strength in the gas chromatogram.

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[9] S. HAYASHI, A. MATSUO and T. MATSUURA, *Experientia* **25**, 1139 (1969).
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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**

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(*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).