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FATTY ACID ETHYL ESTERS IN THE LIVERWORT *CONOCEPHALUM CONICUM*

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Abstract—A series of fatty acid ethyl esters ranging from C_{14} to C_{24} was isolated from a hexane extract of the liverwort *Conocephalum conicum*, these esters accounted for 77% of the extract. The ethyl esters consisting of even-numbered fatty acids were predominant and ethyl palmitate was the major constituent.

INTRODUCTION

In the course of our continuing investigation on chemical constituents of liverworts (Hepaticae), many sesqui- and diterpenoids were isolated. From our experimental investigation of the structures and absolute configurations, almost all of these terpenoids have been shown to be enantiomeric with those from higher plants [1–8]. Additionally, we reported the isolation of fatty acid Me esters and aromatic acid esters as major components from the liverworts, *Pellia fabbroniana* [9] and *Isotachis japonica* [10], respectively.

The present paper deals with the isolation of a series of Et esters of fatty acids as the main component of the hexane-extracted substances of *Conocephalum conicum* (L.) Dum., a thalloidal liverwort belonging to the Conocephalaceae (Marchantiales).

RESULTS AND DISCUSSION

The plant was digested with hexane and the solvent was removed under reduced pressure to give a greenish oily substance in a yield of 0.4% of the dried material. GLC of the extract showed 2 major and 9 minor peaks.

The chief component (peak 3) was isolated from the extract by chromatography on Si gel. The IR and ^{1}H NMR spectra exhibited bands due to ester bonding at ν 1740, 1246, 1185 and 1040 cm^{-1} and signals at δ 0.85 (6H, *t*, $J = 7$ Hz), 1.25 (26H, *br s*), 2.21 (2H, *t*, $J = 7$ Hz) and 4.11 (2H, *q*, $J = 7$ Hz) indicating an Et ester of a saturated fatty acid. The MS gave M^+ at *m/e* 284 (5%) and fragment ions at *m/e* 73 (11%), 88 (100), 101 (45), 157 (8) and 239 (4). On the basis of the spectroscopic evidence the main constituent was identified as Et hexadecanoate. Other peaks in the GLC were identified as a series of Et esters of fatty acids ranging from C_{14} to C_{24} by applying a linear relationship between R_t and C No. All components were, furthermore, confirmed by GC–MS analysis (see Table 1). The relative concentrations of the components are shown in Table 1.

Table 1. Chemical constituents of the hexane extract from *C. conicum*

GLC peak No.	Components	(%)*
1	Et tetradecanoate	2.5
2	Et pentadecanoate	1.8
3	Et hexadecanoate	42.9
4	Et heptadecanoate	3.6
5	Et octadecanoate	32.9
6	Et nonadecanoate	4.9
7	Et eicosanoate	2.5
8	Et heneicosanoate	3.6
9	Et decosanoate	1.8
10	Et tricosanoate	3.0
11	Et tetracosanoate	0.5

* The ratios of the chemical constituents were calculated by GLC from their relative peak area.

Although Et esters of fatty acids have been found in some animal tissues [11–16] and micro-organisms [17], the isolation of the esters from the plant kingdom are confined to some fruits as aroma constituents [18, 19] and in Greek tobacco as flavour components [20]. This is the first time that fatty acid Et esters have been reported from a liverwort.

EXPERIMENTAL

^{1}H NMR spectra were recorded at 60 MHz in $CDCl_3$ soln. GLC analysis was carried out with a FID instrument fitted with a column (300 × 0.3 cm) packed with 3% SE-30 on

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Chromosorb AW. The oven temp. was programmed from 130 to 250° at 5°/min and N_2 was used as carrier.

Material and extraction. C. conicum was collected in the suburbs of Iwakuni City in Yamaguchi Prefecture. After air-drying for a few days, the plant (350 g) was digested with hexane at room temp. The hexane soln was concd *in vacuo* to give a greenish viscous extract (1.4 g).

Isolation of major constituent. The extract (1 g) was chromatographed on a Si gel column (42 × 1.7 cm) using hexane–EtOAc (19:1). From the middle fraction a mixture of esters was obtained (77% of the extract), and this part was re-chromatographed to afford the major constituent in a homogeneous state GLC (SE-30) and TLC (R_f 0.68, hexane–EtoAc, 17:3).

GC–MS of minor constituents. GC–MS analysis of the Et ester fraction was carried out using a silanized glass column (200 × 0.3 cm) packed with 3% SE-30 on Gas Chrom Q. The He flow rate was 25 ml/min, and the oven temp. was programmed from 130 to 240° at 3°/min. MS were determined at 70 eV at an ion source temp. of 310° and a separator temp. of 250°.

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