the structure **1** for 2,3-diacetyl dimethyl barrigenate. The NMR spectrum of the triacetate was also in agreement.

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THE OCCURRENCE OF 24-METHYLENELANOST-8-EN-3β-OL IN THE SEEDS OF *BRASSICA NAPUS*

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Key Word Index—*Brassica napus*; Cruciferae; triterpene alcohol; 24-methylenelanost-8-en-3β-ol; seeds.

Plant and source. The seeds of *Brassica napus* were courteously supplied by Dr. A. Nishioka, Toyo Oil Manufacturing Co., Chiba, Japan. *Uses.* The seeds are widely used for the production of rape-seed oil. *Previous work on 4,4-dimethylsterols (triterpene alcohols).* Cycloartanol [1], cycloartenol [1–4], 24-methylenecycloartanol [1–4], α-amyrin [2,3], β-amyrin [1–3], butyrospermol [3,4] and lupeol [3] in the commercially available rape-seed oil produced from the seeds of *Brassica* spp.

Present work. Extraction of the dried and ground seeds of *B. napus* (158 g) by CH_2Cl_2 using a Soxhlet apparatus gave a dark brown oil (64 g). The unsaponifiable fraction (1.22 g) extracted from the oil after saponification was fractionated by PLC on Si gel using hexane–Et_2O (4:1) as the developing solvent [1], to give the 4,4-dimethylsterol fraction (36 mg). On acetylation, the acetate fraction (33 mg) obtained was separated into two principal bands (R_f 0.39 and 0.24) by PLC on $AgNO_3$–Si gel (1:9) using CH_2Cl_2–CCl_4 (1:1) as the developing solvent. The acetate fraction (6 mg) recovered from the R_f 0.24 band gave two GLC peaks: The GC–MS for the faster eluted minor peak (20%) gave M^+ at *m/e* 482 ($C_{33}H_{54}O_2$) with fragment ions at *m/e* 467 (Table 1, ion a) and 407 (c) indicating that this compound was the acetate of a C_{31} triterpene alcohol. Ions at *m/e* 297 (d) and 301 (e) showed that the side chain had nine carbon atoms and one double bond. An ion at *m/e* 383 (g) indicated the presence of a 24-methylene group [5,6] in sterol devoid of the 9β,19-cyclopropane ring [6], and the ion e indicated the presence of a methyl group attached at C-14 [7]. The GLC and MS data of this triterpene acetate were identical with those measured for the acetate of 24-methylenelanost-8-en-3β-ol occurring in the acetylated 4,4-dimethylsterol fraction separated from an yeast, *Pichia* sp. [8]. The slower eluted major peak (80%) was identified as the acetate of 24-methylenecycloartanol by comparison of its GLC and MS data with those of the authentic specimen of 24-methylenecycloartanyl acetate [9]. The hydrogenated fraction (PtO_2 catalyst, Et_2O soln) afforded two constituents which had the GLC and MS data identical with those of the authentic specimens [9] of the acetates of 24-methyllanost-8-en-3β-ol and 24-methylcycloartanol, respectively.

Thus, 24-methylene-5α-lanost-8-en-3β-ol occurs as a

Table 1. GLC and MS data of triterpene acetates.

	GLC data RR_t (sitosterol = 1.00)			MS data (in GC–MS, 70 eV), *m/e* (>200) and relative intensities (%)							
	SE-30*	OV-17†	OV-225‡	M^+	a§	b	c	d	e	f	g
24-Methylenecycloartanyl acetate	1.77	1.67	1.45	482 (16)	467 (14)	422 (100)	407 (84)	297 (34)	301 (14)	300 (36)	—
24-Methylcycloartanyl acetate	1.82	1.62	1.37	484 (18)	469 (24)	424 (100)	409 (90)	297 (59)	—	302 (56)	—
24-Methylenelanost-8-en-3β-yl acetate	1.56	1.41	1.20	482 (39)	467 (100)	—	407 (89)	297 (6)	301 (28)	—	383 (11)
24-Methyllanost-8-en-3β-yl acetate	1.61	1.37	1.13	484 (20)	469 (100)	424 (7)	409 (98)	297 (7)	301 (7)	—	—

* 3% SE-30; 238°, N_2 50 ml/min. † 3% OV-17; 268°, N_2 50 ml/min. ‡ 10% OV-225; 260°, N_2 50 ml/min. § Major fragment ions: a, M^+–Me; b, M^+–AcOH; c, M^+–Me–AcOH; d, M^+–SC–AcOH; e, M^+–SC–56; f, M^+–ring A [6]; g, M^+–Me–84.

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minor companion of 24-methylenecycloartanol in the 4,4-dimethylsterol fraction from the seed oil of *B. napus*.

Significance. This appears to be the first record of the detection of 24-methylenelanost-8-en-3β-ol in higher plants. This triterpene alcohol has so far been identified only in fungi [8,10,11] among the plant kingdom. The co-occurrence of the Δ^8-triterpene with the 9β,19-cyclopropyl isomer, 24-methylenecycloartanol, in the seed of *B. napus* suggests that the enzymatic opening of the 9β,19-cyclopropane ring may occur at the 4,4-dimethylsterol level. The presence of lanosterol and 24-dihydrolanosterol was recently demonstrated in the seeds of *Capsicum annuum*, Solanaceae [12]. These facts may suggest that the tetracyclic Δ^8-triterpene alcohols are of wide occurrence in higher plants though mostly as the minor triterpene consitiuents.

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CONSTITUENTS OF THE BASIDIOMYCETE *SCLERODERMA AURANTIUM*

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Key Word Index—*Scleroderma aurantium*; Basidiomycetes; fatty acids; steroids; lanostanediols.

Abstract—The following compounds were isolated from the extract of the fresh peridium of *Scleroderma aurantium*: palmitic acid, linoleic acid, a mixture of triglycerides, an ester of a steroidal diol, ergosterol, ergosterol peroxide, 9(11)-dehydroergosterol peroxide, lanosta-8,23-dien-3β,25-diol, lanosta-8,24-diene-3β,23-diol, and mannitol.

INTRODUCTION

The metabolites of the Basidiomycete *Scleroderma aurantium* have been examined by several authors. Zellner [1] reported the isolation of fumaric acid, glycerol, and mannitol. In the extract of the dried peridium, Entwistle and Pratt [2,3] identified a previously reported crystalline substance [1,4] as (23*S*)-lanosta-8,24-diene-3β,23-diol. This diol is labile towards acids and its side chain undergoes allylic rearrangement with the formation of lanosta-8,23-diene-3β,25-diol [5]. The minor components of the extract are assumed to be artefacts formed by the action of acids [2].

RESULTS AND DISCUSSION

In this paper we report the isolation and identification of constituents of the fresh peridium collected in the neighbourhood of Soběslav in Bohemia (Czechoslovakia). Young peridium was used which had a white to light purple belly. As indicated by TLC of the acetone extract, more than the four components previously reported [2] were present and the content of the main component was lower than the 98% previously claimed. In order to prevent the potential formation of artefacts by the action of the acids present, the crude extract was treated with diazomethane to esterify the acids. The methylated extract was concentrated and separated by a combination of column chromatography on Si gel, PLC on Si gel, and GLC. The isolated compounds are considered below according to their increasing polarity on Si gel TLC.

As indicated by MS and GLC, the least polar fraction represented a 3:7 mixture of methyl palmitate and methyl linoleate.

The subsequent oily fraction exhibited in the IR spectrum ester bands (1730 and 1168 cm^{-1}) and C=C bands