arylmagnesium bromides using the previously published method [2] and were recrystallised from ethanol.

The syntheses of the 4-phenyl and 4-methoxyphenyl derivatives have already been reported.[2,3]

The 4-propyl derivative: reaction time 15 min. M.p. 45–46 °C. (Found: C 68.63; H 6.93. Calc. for $C_{15}H_{18}O_4$: C 68.69; H. 6.92.)

The 4-isopropylderivative: reaction time 15 min. M.p. 81.5–82.5 °C. (Found: C 68.67; H 7.00. Calc. for $C_{15}H_{18}O_4$: C 68.69; H 6.92.)

The 4-*o*-tolyl derivative: reaction time 15 min. M.p. 145.5–146.5 °C. (Found: C 73.51; H 5.80. Calc. for $C_{19}H_{18}O_4$: C 73.53; H 5.85.)

The 4-mesityl derivative: reaction time 20 min. M.p. 123.5–125.5 °C. (Found: C 74.32; H 6.53. Calc. for $C_{21}H_{22}O_4$: C 74.52; H 6.56.)

The 4-*o*-*t*-butylphenyl derivative: the ratio of ester to Grignard reagent was increased to 1:5; reaction time 48 h. M.p. 106–107 °C. (Found: C 75.21; H 6.79. Calc. for $C_{22}H_{24}O_4$: C 74.98; H 6.86.)

The 4-methyl derivative: reaction time 15 min. The compound did not crystallise. After careful evaporation of the solvent, the remaining oil gave an excellent NMR spectrum that showed that the reaction product was ethyl 4-methyl-3,4-dihydro-3-coumarincarboxylate.

The unsubstituted ethyl 3,4-dihydro-3-coumarincarboxylate was prepared by esterification of 3,4-dihydro-3-coumarincarboxylic acid in ethanol in the presence of dry hydrogen chloride. The reaction product did not crystallise but after careful evaporation of the solvent gave an excellent NMR spectrum that showed that it was ethyl 3,4-dihydro-3-coumarincarboxylate.

3,4-Dihydro-3-coumarincarboxylic acid was prepared from 3-coumarincarboxylic acid [4] by reduction with sodium amalgam according to the method used in the synthesis of *N*-methyl-3,4-dihydroxyphenylalanin.[5] The melting point, 141–142 °C, agrees with the value given in the literature.[6]

1. Holmberg, G. A., Malmström, F. and Wennström, U. *Acta Chem. Scand. 27* (1973) 2023.
2. Holmberg, G. A. *Acta Chem. Scand. 15* (1961) 1255.
3. Holmberg, G. A. and Johansson, J. E. *Acta Acad. Åbo B 30* (1970) No. 13.
4. Knoevenagel, E. *Ber. Deut. Chem. Ges. 31* (1899) 2385.
5. Deulofeu, V. and Guerrero, T. J. *Org. Syn. Coll. Vol. 3* (1955) 586.
6. Dean, F. M., Robertson, A. and Whalley, W. B. *J. Chem. Soc.* (1950) 895.

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5α,8α-Peroxyergosteryl Divaricatinate from *Haematomma ventosum*

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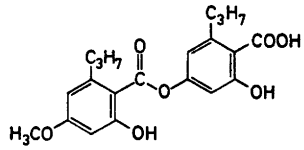
The crystalline material from *Haematomma ventosum* (L.) Mass. (for details, see Experimental) gave a mass spectrum which exhibited two important fragmentations. One corresponded to the elimination of divaricatinic acid, to give a fragment of composition as ergosterol peroxide which had lost one molecule of water. The other fragmentation corresponded to a further loss of O_2. The observed light absorption of the isolated material, *cf.* Table 1, was very similar to that of methyl divaricatinate,



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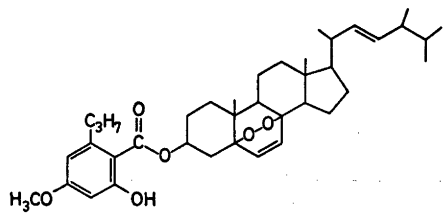

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which may be obtained from divaricatic acid (*1*), a depside which has been isolated from *H. ventosum*.[1] The correctness of the idea that the isolated substance would be peroxyergosteryl divaricatinate (*2*) was shown by partial synthesis. The synthetic and natural materials showed identical UV, IR, and mass spectra, no depression of m.p. on admixture, and a similarly low optical activity.

Whilst peroxyergosterol has been isolated from natural sources on several occasions, so far mainly from lichens,[2,3] this appears to be the first time an ester of it has been reported.

Experimental. IR spectra in KBr were recorded on a Perkin-Elmer Model 257 spectrometer, UV spectra on a Hitachi 124 spectrometer,

Table 1. UV light absorption of isolated and synthetic peroxyergosteryl divaricatinate and of methyl divaricatinate.

Peroxyergosteryl divaricatinate				Methyl divaricatinate	
Isolated Max.	ε	Synthetic Max.	ε	Max.	ε
302	6 000	301	5 500	303	5 000
264	14 500	263	14 000	263	15 500

mass spectra on an AEI MS902 instrument, and ^{1}H NMR spectra on a Varian A-60A spectrometer.

The material (4.48 kg) was collected in the Oppdal region some 140 km south of Trondheim. It was extracted for 24 h with ether in a glass Soxhlet apparatus. The neutral part (20.3 g) of the material was obtained by extracting the acidic substances with alkali. It was chromatographed on alumina (600 g). The material eluted with ether and ether-methanol 9:1 (3.7 g) was rechromatographed on silica gel, 400 g, retention volume 700 ml. After 800 mg had been eluted with benzene (700 ml) and benzene-ether 99:1 (2100 ml), 162 mg were eluted with the first 700 ml of benzene-ether 49:1. It slowly deposited *crystals*, which, recrystallised from acetone, melted at 171 – 172 °C, $[\alpha]_D$ + 1° (*c* 1.00, 1 dm tube, $CHCl_3$). M^+ at *m/e* 620 (11 %), found 620.4073, calculated for $C_{39}H_{56}O_6$ 620.4077; *m/e* 410 (10 %), $C_{28}H_{42}O_2$; *m/e* 378 (100 %), $C_{28}H_{42}$. The IR spectrum had bands at 3500 – 3000 cm^{-1} (OH) and at 1643 cm^{-1} (C=O). UV spectrum, see Table 1. The ^{1}H NMR spectrum had a singlet at δ 3.80 (OCH_3) and a multiplet at 5.23 (olefinic proton) as the two most interesting features.

Ergosteryl peroxide was prepared according to Windaus and Brunken,[4] m.p. 176 – 177 °C, reported 178 °C.

Divaricatinic acid chloride was prepared with oxalyl chloride according to Adams and Ulich.[5] Divaricatinic acid (250 mg) in dry benzene (10 ml) was cooled in ice-water and oxalyl chloride (1.5 ml) was added. After 40 min at room temperature benzene and excess oxalyl chloride were removed in a vacuum whilst nitrogen was passed through.

Peroxyergosteryl divaricatinate. Peroxyergosterol (0.5 g) in dry benzene (10 ml) and redistilled dry pyridine (5 ml) was added dropwise to crude divaricatinic acid chloride. After standing for 18 h the mixture was heated for 1 h on the water bath. The cooled mixture was diluted with ether and extracted with 2 N sulfuric acid, sodium carbonate and water. The residue (0.66 g) was chromatographed on silica gel (60 g). Elution with benzene-ether 99:1 gave a substance which was crystallised from acetone to give long, colourless needles (30 mg), m.p. 169 – 170 °C, $[\alpha]_D$ + 5° (*c* 2.00, 1 dm tube, $CHCl_3$).

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1. Culberson, C. F. *Chemical and Botanical Guide to Lichen Products*, The University of North Carolina Press, Chapel Hill 1969, p. 355.
2. Takahashi, R., Tanaka, O. and Shibata, S. *Phytochemistry 11* (1972) 1850.
3. González, A. G., Martín, J. D. and Melián Martín, M. *An. Quim. 69* (1973) 807.
4. Windaus, A. and Brunken, J. *Justus Liebigs Ann. Chem. 460* (1928) 225.
5. Adams, R. and Ulich, L. H. *J. Amer. Chem. Soc. 42* (1920) 599.

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Correction to "Tobacco Chemistry. 22"*

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The configurational designation of one of the title compounds, (1′*S*,6′*S*)-4-(2′,2′,6′-trimethyl-6′-vinylcyclohexyl)-2-butanone, is incorrect and its name should read (1′*S*,6′*R*)-4-(2′,2′,6′-trimethyl-6′-vinylcyclohexyl)-2-butanone. The structure and stereochemistry of the compound, and the formula given, corresponding to the latter name, are reproduced correctly.

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