

Table 1. Moss hydrocarbons

Moss	Alkanes									Hopene-b	9(11)-Farnene	Others
	C ₂₅	C ₂₆	C ₂₇	C ₂₈	C ₂₉	C ₃₀	C ₃₁	C ₃₂	C ₃₃			
<i>B. rivulare</i>	1.0	1.2	1.4		8.4		5.5			69.5		13.0
<i>Ca. introflexus</i>	2.0	0.8	8.2	1.3	18.9	3.0	33.9	1.4	0.3	20.6		9.6
<i>Ct. molluscum</i>	7.0	1.4	20.9	0.3	9.4		6.3			54.7		
<i>R. lanuginosum</i>	2.2	1.5	9.5	6.1	31.9	2.5	24.1	1.5	20.3			0.4
<i>S. touretii</i>	5.2	1.2	28.1	0.7	12.3	0.8	16.4	0.3	33.1		1.9	

Table 2. Triterpenoid alcohols and sterols

Moss	Ergosterol	Stigmasterol	Campesterol	Sitosterol	Obtusifolol	Cyclo-eucalenol	31-Norcyclo-laudenol	Cyclo-laudenol	Others
<i>B. rivulare</i>	27.6	5.9		57.7		8.7	0.1		
<i>Ca. introflexus</i>	20.8	5.5	1.7	29.1		37.7		0.6	4.6
<i>Ct. molluscum</i>	24.2	18.6		54.4					2.8
<i>R. lanuginosum</i>		13.8	5.7	2.9	47.8		26.3	3.5	
<i>S. touretii</i>		25.0	4.1	54.2		11.8		0.7	4.2

Table 3. Fatty acids

Fatty acid	Moss*					
	1	2	3	4	5	6
Palmitic	19.7	22.3	8.5	28.7	10.6	25.2
Palmitoleic	2.4	12.7	2.9	5.0	3.0	4.4
Heptadecanoic			0.3		0.5	0.1
Heptadecenoic	1.2	0.7	3.4	0.6	1.0	0.2
Stearic	2.7	1.4	0.2	1.9	0.7	1.2
Oleic	6.4	5.4	6.6	7.5	10.3	5.6
Linoleic + nonadecanoic	32.7	11.5	44.4	17.3	16.7	14.7
Linolenic + arachidic	11.3	11.5	23.3	15.5	50.2	19.7
Nonadecenoic	1.0	1.0	1.5	2.0	1.2	1.0
Gadoleic	4.0	9.0	3.1		2.8	2.3
Eicosadienoic	0.8		1.1	5.3		2.7
Behenic	15.2	16.8	3.9	13.7	3.0	14.4
Lignoceric	2.5	7.7	0.8	2.5		8.5

* Key: 1, *A. viticulosus*; 2, *B. rivulare*; 3, *Ca. introflexus*; 4, *Ct. molluscum*; 5, *R. lanuginosum*; 6, *S. touretii*.

mitrium lanuginosum (Hedw.) Brid.; *Scleropodium touretii* (Brid.) L. J. Koch.

RESULTS

Tables 1–3. Data from GLC analyses directly or on methyl esters in the case of the fatty acids.

EXPERIMENTAL

(For details, see refs. [1] and [2]). Obtusifolol (identity con-

firmed by mp, mp of acetate, specific rotation, NMR and MS) was separated from the other alcoholic constituents of *Racomitrium* by chromatography over neutral alumina (eluants, light petrol–Et₂O, 1:1). Analysis of the crude alcoholic fraction by GLC and IR (as done for other mosses) was not suitable for the identification of the compound, since it had the same retention time as sitosterol on two columns, and its IR spectrum was almost indistinguishable from the spectra of the other tetracyclic triterpenic alcohols containing a methylene group in the side chain. It appears possible, therefore, that other mosses may contain obtusifolol, whose isolation from this moss seems to be in agreement with the view that it is an intermediate in the biotransformation of tetracyclic triterpenes into phytosterols [3]. The presence of hopane derivatives in mosses further confirms the phylogenetic relationship between bryophytes and pteridophytes.

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REFERENCES

1. Marsili, A. and Morelli, I. (1968) *Phytochemistry* 7, 1705.
2. Marsili, A. and Morelli, I. (1970) *Phytochemistry* 9, 651.
3. Benveniste, P., Hewlins, M. J. E. and Fritig, B. (1969) *European J. Biochem.* 9, 526.

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BRASSICASTEROL IN *CLADONIA GONECHA* AND *STEREOCAULON TOMENTOSUM*

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Key Word Index—Lichens; *Cladonia gomecha*; *Stereocaulon tomentosum*; brassicasterol.

Plants. *Cladonia gomecha* (Ach.) Asah. Cladoniaceae, grown on peat bog; *Stereocaulon tomentosum* Fr., Stereocaulaceae, grown on rock, both from the Agle-Lurudal

region. Until recently *Cladonia deformis* (L.) Hoffm. and *C. gomecha* (Ach.) were considered varieties of the same species, *C. deformis*. They are now [1] treated as well

separated distinct species. Voucher specimens of the samples previously investigated in this laboratory [2,3] have been redetermined and found to be of *C. gonecha*. The determination of the lichen used in this investigation and the redeterminations were done by Mr. H. Østhagen Botanisk Museum, Oslo.

Previous investigations. *C. gonecha*: Bellidiflorin, squamatic acid, usnic acid, rhodocladonic acid [4]. *S. tomentosum*: Atranorin, lobaric acid, stictic acid, [4, p. 522], bourgeanic acid [5].

Present investigation. Brassicasterol has been isolated from both the lichens examined and identified by mp. of the compound and its acetate and by MS. To ensure authenticity of origin, specimens of *C. gonecha* were picked individually, whilst *S. tomentosum* occurred in a pure or almost pure stand. Check on purity therefore mostly consisted in removal of plant debris.

EXPERIMENTAL

Stereocaulon tomentosum. For origin of the material, see [5]. The dried neutral fraction (15 g) was chromatographed on Al_2O_3 to give 10.3 g of dark coloured mass eluted with Et_2O -MeOH (9:1), which slowly deposited colourless crystals, isolated with MeOH (60 mg). Recrystallised from $CHCl_3$ -MeOH; mp 146–147°, $[\alpha]_D^{25}$ –63° (c. 1.47, $CHCl_3$), no selective absorption above 220 nm; acetate, mp 151–152° from MeOH, $[\alpha]_D^{25}$ –65° (c. 1.00). Observed data were in agreement with those reported for brassicasterol and its acetate [6]; MS identical with published MS [7].

Cladonia gonecha. Origin of the material, see [2]. Usnic acid, $[\alpha]_D^{25}$ –480° (c. 1.11); rotation not reported in [4]. The neutral fraction (30.5 g) was chromatographed on Al_2O_3 . Et_2O eluted 2.1 g, which was acetylated and crystallised to give brassicasterol acetate, mp 152–153° from petrol (bp 40–70°); $[\alpha]_D^{25}$ –63° (c. 1.50), undepressed on admixture with the acetate above; their MS were identical. More recently another sample from the same locality (1.0 kg) furnished 6.2 g of neutral material. Chromatographed on Si gel elution with C_6H_6 - Et_2O (3:1) afforded a late, viscous fraction (153 mg) which gave 22 mg of crude brassicasterol, recrystallised from MeOH, mp 142–143°, no depression on admixture with brassicasterol; their MS were identical.

REFERENCES

1. e.g. Dahl, E. and Krog, H. (1973) *Macrolichens of Denmark, Finland, Norway and Sweden*, p. 63, Universitetsforlaget, Oslo, Bergen, Tromsø.
2. Bruun, T. and Sørensen, N. A. (1954) *Acta Chem. Scand.* **8**, 703.
3. Bruun, T. (1954) *Acta Chem. Scand.* **8** 1841.
4. Culberson, C. F. (1969) *Chemical and Botanical Guide to Lichen Products*, p. 313, The University of North Carolina Press, Chapel Hill.
5. Bruun, T. (1973) *Acta Chem. Scand.* **27**, 3120.
6. *Elsevier's Encyclopedia of Organic Chemistry* (Radt, F., ed.) (1954) Series II, Vol. 14, Supplement, p. 1757, Elsevier, Amsterdam.
7. Idler, D. R. and Wiseman, P. (1971) *Comp. Biochem. Physiol.* **A38**, 581, see p. 586.

Phytochemistry, 1976, Vol. 15, pp 1180–1182 Pergamon Press Printed in England.

POLYPHENOLS OF *EUCALYPTUS GLOBULUS*, *E. REGNANS* AND *E. DEGLUPTA*

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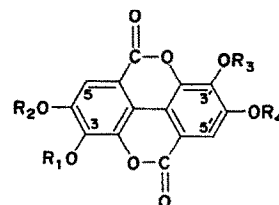
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Key Word Index—*Eucalyptus*; *E. globulus*; *E. regnans*; *E. deglupta*; Myrtaceae; 3-mono-*O*-methyl ellagic acid-4'-rhamnoside, methylellagic and ellagic acids.

Eucalyptus deglupta Blume (Myrtaceae, "Kamarere"), *E. globulus* Labill ("Blue Gum") and *E. regnans* F. Muell ("Mountain Ash") are fast-growth species in appropriate climate zones.

The amount of MeOH solubles in both bark and wood from young trees of *E. globulus* and *E. regnans* and the composition of the wood extractives of both species is very similar (Table 1). Chromatographic examination of *E. globulus* bark extractives revealed at least 10 major components excluding polymers (Table 1). The ellagitannins D-1, D-2, D-6 and D-13, catechin and ellagic (1a) and gallic acids were identified. Proanthocyanins were present in only very small amounts. A new compound 3-*O*-methylellagic acid-4'-rhamnoside (1b), β -diketone(tritriacontane-16,18-dione), calcium oxalate and chlorogenic acid were isolated and identified from their physical and spectral data, and the preparation of derivatives. 1b was hydrolyzed to 3-*O*-methylellagic acid and rhamnose in equimolar proportions. Methylation fol-

lowed by hydrolysis yielded 3,4,3'-tri-*O*-methylellagic acid (1c), the NMR spectrum of 1b indicated that it is an α -rhamnopyranoside.



- (1a) $R_1, R_2, R_3, R_4 = H$
 (1b) $R_1 = Me, R_2, R_3 = H; R_4 = \text{rhamnosyl}$
 (1c) $R_1, R_2, R_3 = Me; R_4 = H$
 (1d) $R_1, R_3 = Me; R_2, R_4 = H$
 (1e) $R_1, R_2, R_3, R_4 = Me$

The most notable features of the extractives in the samples of *E. deglupta* collected in New Britain, New