(5–10 mg) as described in ref. [9]. The extract was extensively dialysed and the material retained in the dialysis tubing rotary evaporated to dryness and hydrolysed by TFA.

Gas chromatography. Monosaccharides and uronic acids were analysed as their alditol acetates as described in ref. [10] Sugar standards were subjected to TFA hydrolysis before use. Alditol acetates were separated isothermally at 215° on packed columns (3 m × 4 mm) packed with 3% SP2330, with N_2 at 25 ml/min as carrier gas and a FID Identification and quantification of hexitol acetates derived from uronic acids was confirmed using a capillary column (WCOT with CP Sil 5 liquid phase, 0.14 μm film thickness), 25 m × 0.23 mm, temp. programmed from 190° to 230° at 5°/min; an FID was used, with an injection vol of 1 μl and a split ratio of 50:1; the carrier gas was N_2 at 1 ml/min.

Lignin analysis Lignin was analysed by the method of ref. [11] as modified in ref [6] Cell wall material (8–10 mg) was extracted for 16 hr with 1 ml 0.5 M NaOH at 70°. The material was centrifuged at 10000 *g* for 1 min and the pellet washed twice with 1 ml H_2O Supernatant and washings were combined, neutralized to pH 8 5–9.0 with 1 M HCl and made up to 4 ml with H_2O. Samples (0.4 ml) were diluted to 2 ml either with 0.05 M NaOH or with 0 05 M NaPi buffer, pH 7, and analysed by UV spectroscopy within 3 hr

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POLYSACCHARIDE OF THE RED ALGA *RISSOELLA VERRUCULOSA*

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Key Word Index—*Rissoella verruculosa*; Rhodophyceae; κ-carrageenan; neocarrabiose unit; neocarrabiose sulphate unit.

Abstract—The Mediterranean red alga, *Rissoella verruculosa*, contains a κ-like carrageenan. ^{13}C NMR studies indicate that the polysaccharide contains neocarrabiose sulphate units alternating with non-sulphated neocarrabiose residues.

INTRODUCTION

In a previous paper we reported on the sterol content of *Rissoella verruculosa* [1] which is the most abundant red alga of the Mediterranean French coast near Banyuls-sur-Mer. In view of the possible economic value of this alga, we have determined the chemical composition of its polysaccharide.

RESULTS AND DISCUSSION

Rissoella verruculosa is an annual seaweed. The yields of polysaccharide are particularly high and remain unchanged (50%/dry wt) from April to July. Acid hydrolysis of the polysaccharide gave the following monosaccharides (% total): galactose (91.8), xylose (2.7), mannose (0.6) and glucose (4.9). An $[\alpha_D]$ of +12.5° for the polysaccharide and its IR spectrum suggested a D-configuration for 4-*O*-linked, 3,6-anhydro-α-galactopyranose units (A-unit) alternating with 3-*O*-linked β-D-galactopyranose (G-unit) units as found in κ-carrageenan (Fig. 1). The IR spectra were quite similar to those of a commercial sample of κ-carrageenan with absorptions at 930 cm^{-1}, indicating 3,6-anhydrogalactose units, and 840 cm^{-1}, indicating 4-sulphate groups on galactose units (Fig. 2).

The chemical composition of the galactan of *R. verruculosa* is given in Table 1. The polysaccharides obtained after 'normal' and 'high milk reactivity' treatments yielded similar amounts of sulphate, excluding any 6-sulphate-galactose groups (μ-precursor of κ-carrageenan). The 'high milk reactivity' treatment consists of extraction of the alga with a dilute aqueous calcium hydroxide solution. This treatment changes μ-carrageenan into κ-

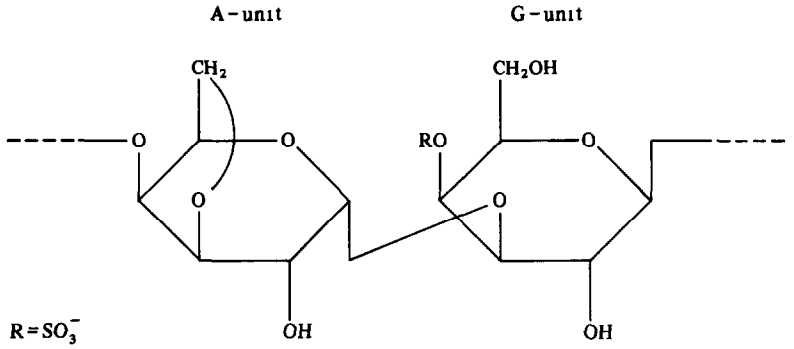

Fig. 1. Disaccharide repeating units in κ-carrageenan.

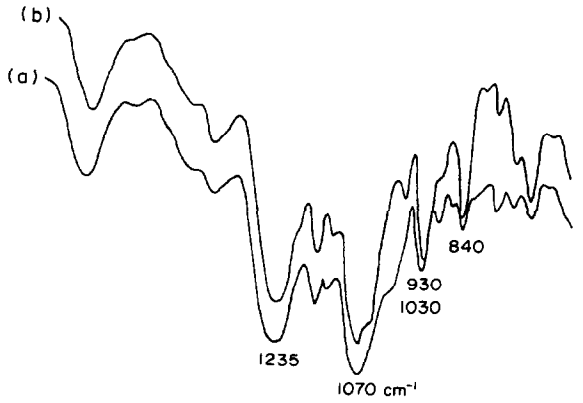

Fig. 2. IR spectra of carrageenan from *R. verruculosa* and commercial κ-carrageenan (SATIA).

carrageenan. ^{13}C NMR spectroscopy can be applied to the analysis of red algal polysaccharides [2]. The range δ95–105, assigned to the anomeric carbon atoms of sugar residues [3], consists of three signals at δ105.3, 97.8 and 97.2 (Fig. 3). The signal at δ105.3 was assigned to G-1 and 97.8 to A-1 of the neocarrabiose sulphate repeating structure (Fig. 1, R = SO_3^-). The signal at δ97.2 was assigned to A-1 of a non-sulphated neocarrabiose unit (Fig. 1, R = H).

So, as previously described for the κ-furcellaran (*Furcellaria fastigata*) and the galactan of *Phyllophora*

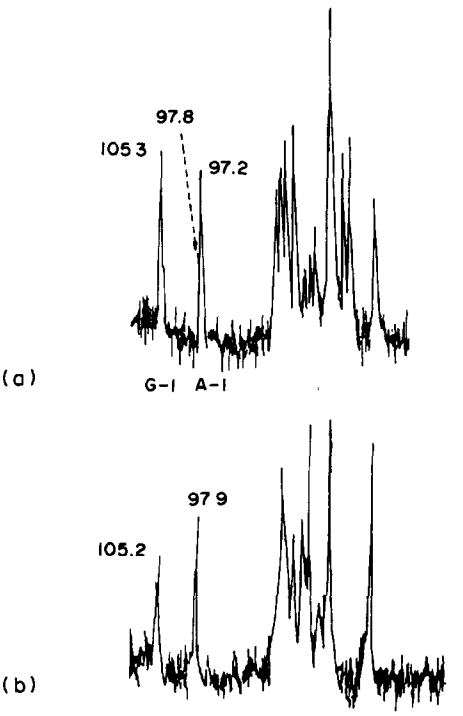

Fig. 3. ^{13}C NMR spectra of carrageenan from (a) *R. verruculosa* and (b) commercial κ-carrageenan (SATIA).

Table 1. Chemical composition (%) of the galactan from *R. verruculosa*

	H_2O	HCO_3^-	Na^+	K^+	Ca^{2+}	SO_4^{2-}	3,6-A-Gal†	Gal	Proteins
NT*	3.3	—	1.0	1.5	1.5	18.5	27.4	27.6	6.4
HMR*	3.2	9.0	.9	1.5	3.6	16.5	25.8	26.2	5.9

*NT, Normal treatment, ashes 18.1%; HMR, High milk reactivity, ashes 16.9%.
†3,6-A-Gal, 3,6-Anhydrogalactose.

nervosa [3], the polysaccharide of *R. verruculosa* contains both neocarrabiose and neocarrabiose sulphate residues.

EXPERIMENTAL

Algal material. Samples of *R. verruculosa* were harvested from April to July at Banyuls-sur-Mer on the Mediterranean French coast.

Extraction. The alga (6 g) was extracted with 600 ml boiling H_2O (NT) or 200 ml 8% $Ca(OH)_2$ [Société Anonyme de Traitement Industriel des Algues, personal communication] soln at 90° (HMR). The polysaccharide was recovered (3 g) by isoPrOH pptn (1500 ml).

Hydrolysis of the polysaccharide and sugar analysis. The polysaccharide (1 g) in 0.5 M H_2SO_4 (5 ml) was totally hydrolysed during 16 hr at 95°. After neutralization with $BaCO_3$, inositol was added as int. standard (200 mg). Sugars were separated by HPLC on Lichrosorb NH_2 (10 μm; 250 × 4 mm) eluted with MeCN–H_2O (4:1, 2 ml/min). Galactose, xylose, mannose and glucose were identified by comparison with authentic samples. Reduction of the sugars with $NaBF_4$, followed by neutralization with HOAc and subsequent acetylation yielded alditol acetates which were analysed by GC on 3% SP 2340 (2 m × 3 mm column at 225°) with a N_2 flow of 18 ml/min. Authentic alditol acetates were used for identification and the different amounts were determined by int. standardization

The 3,6-anhydrogalactose residues were analysed by the colorimetric resorcinol method using fructose for the standardization [4]. The total sugar content was measured by the colorimetric H_2SO_4–PhOH method [5].

IR spectra were recorded from a film prepared by slow evaporation of a 0.4% H_2O soln at 60° on an Afcodur plate. ^{13}C NMR spectra were recorded in D_2O (50 mg/ml) at 95° (62.9 MHz); chemical shifts were measured relative to int. DSS and converted to external TMS.

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LIPIDS FROM THE GLANDULAR TRICHOME OF *AILANTHUS ALTISSIMA*

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Key Word Index—*Ailanthus altissima*; Simaroubaceae; secretory hairs; lipids; fatty acids.

Abstract—The secretion from the glandular trichomes of *Ailanthus altissima* was found to contain bound lipid (mainly monogalactosyldiacylglycerol) as well as oleic, palmitic and linoleic acids in the free state.

In *Ailanthus altissima* (Mill.) Swingle, when buds open, the cataphylls and the stem are covered with different types of stalked secretory hairs: filiform hairs, trumpet-shaped hairs or massive column-shaped hairs [1]. All these correspond to oil glands.

From the secretion the lipid classes were separated by TLC and their fatty acid composition analysed by GC (Table 1). Of total lipids 53.7% consisted of free fatty acids. Monoacylglycerol (MG) and triacylglycerol (TG) were found to be present in low amount. Of the polar lipids, phospholipids were absent and monogalactosyldiacylglycerol (MGDG) represented the major component of glycolipid. The main fatty acids were 18:1 (oleic), 16:0 (palmitic) and 18:2 (linoleic). Oleic acid alone accounted for 51.8% and 73.2% of total fatty acid and free acid, respectively. The literature referring to studies of lipids produced by secretory hairs is scanty; nevertheless, lipids from floral glands of *Krameria* [2] were found to be composed almost entirely of free fatty acids.

EXPERIMENTAL

In spring, cataphylls and stems were collected in opening buds. The material was fixed in boiling H_2O and washed in $CHCl_3$ to extract lipids of the secretion. Total lipids were fractionated into neutral lipids plus glycolipids and phospholipids by TLC [3–4].