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epiFriedelinol and Derivatives, a Re-investigation

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The occurrence of epifriedelinol in *Ceratopetalum apetalum* D. Don (Cunoniaceae)¹ and the lichen *Cetraria nivalis* (L.) Ach.² has recently been reported simultaneously and independently by us. The rotations recorded in the two communications were, however, so widely differing (compare Table 1) that it could not be accounted for by experimental errors alone. The difference could conceivably be due to a small content of a contaminant in one of the samples. To settle this question a re-investigation was undertaken, the details of which are found in the experimental part. We believe that the rotations now found (see Table 1) should be regarded as the correct ones. The differences in the m.p.'s are not significant in view of their range and different measurement conditions.

As is seen from the experimental part, there is a strong indication that epifriedelinol from *Cetraria nivalis* did contain a small amount of some other material, but

further investigations were prevented by lack of material.

Experimental. M.p.s are not corrected. Rotations were measured at room temperature (approximately 20°) in chloroform in a 1 dm tube, unless specified to the contrary.

The epifriedelinol used in these investigations, except in one case, was the original sample obtained from *Ceratopetalum apetalum* D. Don¹, $[\alpha]_D +19^\circ$ (c. 0.91), $+21^\circ$ (c. 1.02), m. p. 272—275°, admixture with a sample of the lichen epifriedelinol (m. p. 273—276°) m. p. 272—276°, all three taken at the same time. Similarly, in evacuated tubes, the m.p.s were, respectively, 280—281°, (281—282°) and 281—282°.

epiFriedelanyl acetate. The acetate was prepared with acetic anhydride in pyridine with standing at room temperature for 4 days in the same way as previously used by Bruun². Sufficient pyridine was used to keep the alcohol in solution. The product was filtered through alumina in benzene and crystallised from chloroform-methanol, m. p. 284—285°, admixture with the original acetate (prepared in the same way) of epifriedelinol from lichens (m. p. 273—274°)² m. p. 270—285°, all three taken at the same time, $[\alpha]_D +37^\circ$ (c. 1.02). Recrystallised the acetate melted at 282—283°, $[\alpha]_D +38^\circ$ (c. 0.96). After drying at 115° for 6 hours in a water-pump vacuum it melted at 282—285°, $[\alpha]_D +34^\circ$ (c. 1.76).

A sample of the acetate was also prepared by refluxing for 1 hour 20 mg of epifriedelinol from lichens with acetic anhydride as used by Jefferies¹. The crystals which deposited on cooling were filtered, m. p. 276—279°, admixture with the previously prepared acetate from lichens (m. p. 271—274°) m. p. 271—274°, all three taken at the same time, $[\alpha]_D +33^\circ$ (c. 1.24). Recrystallised it melted at 281—283°, admixture with the sample above from *Ceratopetalum apetalum* (m. p. 282—285°) m. p. 282—285°, all three taken at the same time, $[\alpha]_D +33^\circ$ (c. 1.11).

Table 1.

	<i>Ceratopetalum apetalum</i> D. Don		<i>Cetraria nivalis</i> (L.) Ach.		Present investigation	
	m.p.	$[\alpha]_D$	m.p.	$[\alpha]_D$	m.p.	$[\alpha]_D$
epiFriedelinol	279—283°	+ 24°	281—282° (vac.)	+ 15°	272—275° 280—281° (vac.)	+ 20°
Acetate	290—294°	+ 45°	275—276° (vac.)	+ 12°	282—285°	+ 35°
Benzoate	254—257°	+ 40°	232—233° (vac.)	+ 25°	246—248°	+ 34°

The acetic anhydride filtrate (immediately above) was decomposed with water and organic material extracted with ether. Acetic acid was removed by sodium hydrogen carbonate solution. Evaporation of the ether left a yellow resin that partly crystallised. The amount was estimated at 2 mg or 10 % of the starting material. From acetone colourless crystals were obtained, which melted at 230—245°. A mixture with *epifriedelanyl acetate* melted at 230—255°.

epiFriedelanyl benzoate. A small sample of the benzoate from the original alcohol from *Ceratopetalum apetalum*¹ was available. It melted at 250—251°, whilst a mixture with the original benzoate from the lichen material (m. p. 231—232°)² melted at 231—245°, all three taken at the same time. A fresh sample of the benzoate was prepared with benzoyl chloride similarly as the acetate, m. p. 251—252°, $[\alpha]_D + 34^\circ$ (c, 2.19), recrystallised, m. p. 245—247°, $[\alpha]_D + 34^\circ$ (c, 2.06). The dried sample (as above) melted at 246—248°, $[\alpha]_D + 34^\circ$ (c, 1.55).

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The Structure of Liquid Carbon Disulphide

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Several investigators have noted a departure from normal behaviour of liquid carbon disulphide. Hildebrand¹ as early as in 1919 found that the internal pressure calculated from the coefficients of expansion and compressibility gave a comparatively low relative value. Benson² observed that the ratio of the density at the boiling point to the density at the critical point was abnormally large. This he concluded to be due to a dense packing in the liquid structure, arising from the chain-forming tendency of sulphur atoms with

available 3d orbitals. Stavely and Tupman³ in a discussion of entropies of vaporization and internal order in liquids, found the entropy of vaporization of liquid carbon disulphide surprisingly low. According to their general theory, a nearly unrestricted rotation or a low degree of order should be expected in such cases. The Kerr effect, however, indicates a considerable degree of hindrance to free rotation in this liquid, as pointed out by Debye⁴.

Information about the structure of liquid carbon disulphide would consequently be of interest. Hence the electronic radial distribution curve has been determined (at 15° C) for this system. A procedure according to Finbak⁵ was employed. The X-ray intensity measurements have been obtained using MoK α -radiation only. For low scattering angles a Guinier camera was used, permitting observations to be made down to $s = 4\pi(\sin\theta/\lambda) = 1.3 \text{ \AA}^{-1}$. The resulting distribution curve is reproduced in Fig. 1. Maxima are found at 1.55 Å, 4.0 Å, 6.5 Å and 7.6 Å. At about 3.1 Å a superimposed peak can be distinguished.

The peaks at 1.55 Å and 3.1 Å obviously correspond to the C—S and S—S distances within the molecule. They agree very well with the results obtained on gaseous carbon disulphide by X-ray diffraction⁶ and electron diffraction^{7,8}.

The remaining peaks reflect the packing of the molecules. In order to interpret these peaks, a model of the liquid structure will be considered. The molecule itself can be regarded approximately as a cylinder, with a radius r and a length $d + 2r$. Here d is the S—S distance within the molecule. A closepacking of these cylinders requires the volume:

$$V = 2\sqrt{3} r^2(2r + d)$$

Inserting in the formula above the observed liquid volume extrapolated to 0° K⁹, r is found to be 1.85 Å. This value equals the van der Waals radius of sulphur, as tabulated by Pauling¹⁰. At room temperature the formula gives r equal to 2.0 Å and a corresponding packing distance of 4.0 Å for the molecules. The largest peak in the experimental distribution curve occurs at just this distance.

The peaks at 6.5 Å and 7.6 Å are more uncertain because of the experimental errors. The "end to end" packing of the molecules should give a peak at about 7.1 Å according to the previous discussion. The second coordination shell is found at 6.9 Å (and 14.2 Å for the "end to end"