CCCCXXXVI.—*The Rotation Dispersion and Circular Dichroïsm of Caryophyllene Nitrosite.*

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Rotation Dispersion.—Deussen (*Annalen*, 1912, **388**, 161) found that caryophyllene nitrosite in benzene had $[\alpha]_D$ + 1626°, and later (*J. pr. Chem.*, 1912, **85**, 487) he showed that this remarkably high value varies considerably with concentration and is always greater for sodium light than for mercury green. The latter observation and the blue colour of the substance led Tschugaev to suggest (*ibid.*, **86**, 547) that it might show the Cotton effect,* *i.e.*, a maximum of rotation on one side of its absorption band and a minimum on the other. To settle this point the author has examined the rotation dispersion of a solution of caryophyllene nitrosite in alcohol. The results obtained are shown in Fig. 1. The rotation reaches a maximum positive value about 6250 Å.U., becomes zero at 6800 Å.U., and is thereafter negative. Subsequent examination of the absorption spectra has revealed a narrow band with its head about 6800 Å.U., thereby confirming Tschugaev's contention.

The caryophyllene nitrosite was prepared essentially as described by Schreiner and Kremers (*Pharm. Arch.*, 1899, **2**, 282); after crystallisation first from alcohol and then from aqueous acetone it melted at 115°. The alcoholic solution for rotation measurements contained 0·3113 g. of caryophyllene nitrosite per 100 g. of solution, and was contained in a 6-cm. tube. The readings were taken at 20° and the solution had $d_4^{20°}$ 0·7932. Eight different colours of light were used. A mercury-vapour lamp supplied the yellow, green,

* This phenomenon was first observed by Cotton (*Ann. Chim. Phys.*, 1896, **8**, 347) with alkaline solutions of copper tartrate and with potassium chromium tartrate.

and violet ones direct, and narrow strips of the spectrum from a Nernst lamp, corresponding to four other fainter mercury lines and to the red hydrogen line, were utilised in the manner described by Patterson (J., 1916, **109**, 1143). Readings were not continued beyond 6908 Å.U.; indeed, some difficulty was experienced in taking this. The values obtained were :

λ	4358	4916	5461	5790	6234	6563	6717	6908
α	0·78°	1·07°	1·71°	2·31°	3·27°	2·06°	0·66°	−0·97°
$[\alpha]$	526°	722°	1154°	1559°	2207°	1390°	459°	−655°

FIG. 1.

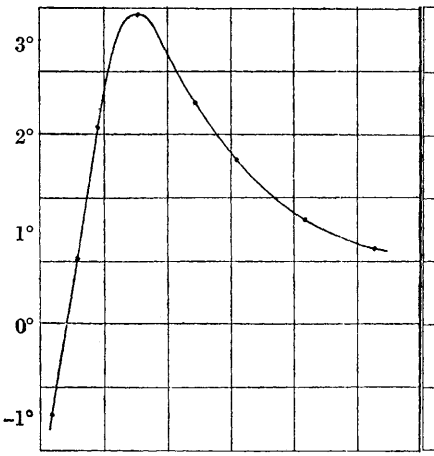
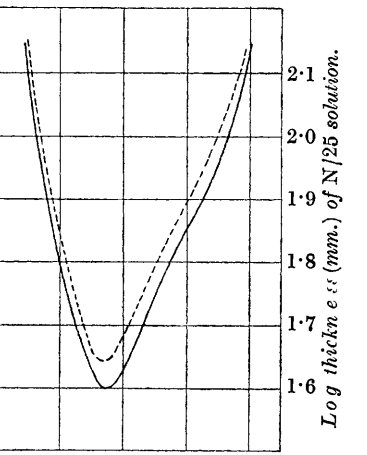


FIG. 2.



——— *Left-handed circularly polarised light.*
- - - - - *Right-handed* ,, ,, ,,

Circular Dichroïsm.—It has been shown by Fresnel that when a beam of plane-polarised light enters a transparent optically active medium it is resolved into two circularly polarised beams (one right-handed and the other left-handed). These travel with different velocities through the medium and combine again on leaving it to give a plane-polarised beam, the plane of polarisation of which is rotated through a certain angle from that of the original beam. Cotton found that in the region of selective absorption the emergent light from his coloured tartrate solutions was elliptically polarised, and he explained this by supposing that, besides travelling at different speeds, the circularly polarised components were absorbed to different extents. This view was subsequently confirmed by direct experiments with right- and left-handed circularly polarised monochromatic light, and by analogy with the dichroïsm of doubly refracting crystals the phenomenon was called circular dichroïsm.

Cotton's work on this subject has been extended to other metallic complexes of tartaric acid and to similar compounds of malic and lactic acids by McDowell (*Physical Rev.*, 1905, **20**, 163), Olmstead (*ibid.*, 1912, **35**, 31), and by Bruhat (*Ann. Physique*, 1915, **3**, 232; 1920, **13**, 36). The last author has also studied the phenomenon with the diphenyldithiourethanes of *d*- and *l*-borneol (*loc. cit.*) and with potassium irido-oxalate (*Bull. Soc. chim.*, 1915, **17**, 223). These, however, appear to be the only cases hitherto recorded, and it is therefore of interest to find a further example in caryophyllene nitrosite.

The above authors have concerned themselves more particularly with the variation of ellipticity (*i.e.*, the ratio of the axes of the elliptical light) with wave-length, but in the present investigation the absorption spectra for right- and left-handed light in the region of selective absorption have been studied. A Fresnel quartz tri-prism (*Ann. Chim. Phys.*, 1825, **28**, 147) was used to produce accurately both right- and left-handed circularly polarised light of equal intensity and contiguous to each other. The centre prism had a refracting angle of 150° and the base was 4″ long. The tri-prism was inserted between the collimator and the prism of a Hilger constant-deviation spectroscope, the collimator being displaced the necessary distance from its usual position. A 500-c.p. Pointolite lamp was employed as source of light. The height of the slit was adjusted with a V-shaped metal slide until the two spectra, produced one above the other by the tri-prism, just ceased to overlap. The Baly tube containing the caryophyllene nitrosite solution ($N/25$ in alcohol) was placed between the light source and the spectroscope slit. The eye-piece of the telescope was then removed and replaced by a single lens and camera, and a series of photographs was taken on a panchromatic plate for different thicknesses of solution. For calibration purposes the Baly tube was removed and a cobalt arc was photographed at the top and at the bottom of the plate. The results are represented graphically in Fig. 2. A distinct difference between the absorption spectra for right- and for left-handed circularly polarised light is apparent.

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