

frequencies, exhibited dichroism corresponding to angles between 32° and 40° .

As a further test of the method, acetanilide was examined by polarized infra-red radiation, and the conclusions reached were checked by an independent X-ray examination kindly made by Mr. D. E. C. Corbridge, of these Laboratories.

In the sample examined, the crystals (space group P_{bca}) formed as needles elongated along the $[b]$ axis and tabular on (100). Most of the bands exhibited a maximum absorption parallel to the $[b]$ axis, but a few, including that at 759 cm^{-1} attributed to the flapping motion of the benzene ring, exhibited a maximum absorption parallel to the $[c]$ axis. From the ratio of maximum to minimum optical densities of the various bands, it was calculated that the benzene rings were inclined at about 20° to the (001) plane, and the projections on (100) of the hydrogen-bonded N—H and C=O bonds were each inclined at about 30° to the $[b]$ axis. From the observed optical densities, it was estimated that the C_6H_5 —N bonds must lie at a fairly small angle to the $[a]$ axis. These conclusions are in agreement with the general arrangement of the molecules as deduced from the preliminary X-ray study.

A further possibility, which has not yet been examined, is to reverse the process and use the infra-red dichroism of crystals of known structure to analyse the infra-red spectra or to check proposed assignments of fundamental frequencies.

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¹ Verweel, H. J., and MacGillavry, C. H., *Z. Kristall.*, A, **102**, 60 (1939).

² Robertson, J. M., *Proc. Roy. Soc.*, A, **150**, 106 (1935).

Oxidation of Neostrychnine

THE action of bromine on neostrychnine, $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2$, in cold acid solution affords a bromohydrobromide transformed by hot water into the hydrobromide of oxodihydroallostrychnine (formerly called oxodihydroneostrychnine), $\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}_2$, in nearly theoretical yield. This substance has now been recognized as an aldehyde, and its formation involves a molecular rearrangement, $:\text{N}:\text{CH}=\text{C}:\rightarrow:\text{N}:\text{C}(\text{CHO}):$. It is noteworthy that the reverse transformation can be realized. Catalytic reduction of the aldehyde in alcoholic solution gives a dihydro-derivative, probably the related primary alcohol; in acetic acid solution an isomeride is produced in addition, and this is converted with great ease by dilute mineral acids into neostrychnine. Nitrous acid transforms neostrychnine into a ketoxime-formamide, $:\text{N}:\text{CH}:\text{C}:\rightarrow:\text{N}:\text{CHO}:\text{HON}:\text{C}:$, which is hydrolysed by dilute hydrochloric acid to hydroxylamine, formic acid and a hydrochloride, $\text{C}_{20}\text{H}_{23}\text{O}_3\text{N}_2\text{Cl}$. This is a salt of a *sec*-basic ketone.

Taking into consideration what is already known in regard to the environment of the basic nitrogen of strychnine, these observations establish the relation of neostrychnine to strychnine. Under the influence of Raney nickel (and in other ways in certain derivatives), the double bond moves just one step in the direction of the basic nitrogen atom. This implies a new view of the methoxylating fission of the metho-salts of the alkaloids.

The direct explanation of the formation of oxodihydroneostrychnine (now termed oxodihydroallostrychnine) and its reconversion to neostrychnine was



and on this basis the older type of formula for strychnine was untenable. The discovery of unexpected and somewhat remarkable molecular rearrangements disposes of this natural explanation. It does not disprove the quinuclidine formula recently proposed¹; but it removes the necessity for its postulation and, in these circumstances, we revert, as the best hypothesis to guide future work, to an earlier suggestion². The relation of this structure to that of cinchonine has already been indicated³. Several slight modifications of this expression are feasible, and these have special advantages and disadvantages which must be discussed at a later date, especially since it is probable that crucial experimental tests can be devised.

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¹ Robinson, R., *Nature*, **159**, 263 (1947).

² Robinson, R., *Experientia*, ii, **1**, 28 (1946). Briggs, I. H., Openshaw, H. T., and Robinson, R., *J. Chem. Soc.*, 903 (1946).

³ Openshaw, H. T., and Robinson, R., *Nature*, **157**, 438 (1946).

Fluorescence of Cancerous and Non-Cancerous Lipids

IN a previous communication, evidence was given¹ indicating the presence in human cancer tissue of a fraction, or fractions, the fluorescent spectra of which were similar to, if not identical with, those produced by methylcholanthrene. The fluorescence produced in a similarly treated lipid fraction obtained from non-cancerous livers was considerably weaker, and appeared in a different region of the spectrum.

These findings were disputed by Hieger², and, in an exhaustive study of lipids obtained from human cancerous and non-cancerous livers, Jones and May³ failed to identify any methylcholanthrene-like compounds in human cancer tissue.

It should be emphasized at the outset that the expression 'methylcholanthrene-like' referred specifically to the similarity of the bands produced by the two substances. However, since even the existence of such bands in cancerous liver lipids was questioned, the present work was undertaken to check the original contention, and to secure a more satisfactory procedure for the isolation and concentration of the material giving the banded fluorescent spectrum. A method was finally developed which has given fairly consistent results. Briefly stated, the procedure is as follows.

The acetone-soluble fraction is obtained as already described⁴. This lipid is then saponified with 10 per cent potassium hydroxide in 70 per cent ethanol in a ratio of 1 : 10 for 24 hours. The ethanol is removed, the residue taken up in ethyl ether, and washed with distilled water until neutral to litmus. The solvent is then removed and the residue resaponified for four hours. The final residue is taken up in acetone and a