THE STRUCTURE OF TRICHLOROCODIDE*

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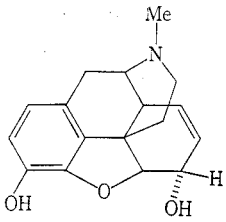
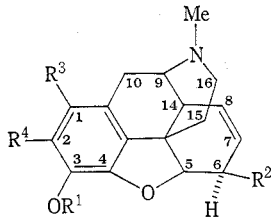
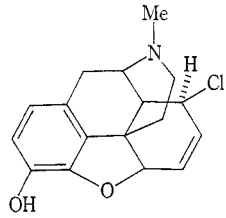
Chlorination of morphine (I) with thionyl chloride gives a high yield of α-chloromorphide (II). Small, Faris, and Malonee[1] found the specific rotation of this product to be much lower than expected and were able to separate small amounts of impurities which were responsible for the low rotation. β-Chloromorphide (III) was obtained in 3% yield and a trichloromorphide in 1·2% yield. The trichloromorphide was methylated to give a trichlorocodide and this original sample was used for the present



(I)



(II) $R^1 = R^3 = R^4 = H$, $R^2 = Cl$
(IV) $R^1 = Me$, $R^2 = R^3 = Cl$, $R^4 = H$
(V) $R^1 = Me$, $R^2 = Cl$, $R^3 = R^4 = H$
(VI) $R^1 = Me$, $R^2 = R^3 = R^4 = Cl$
(VII) $R^1 = H$, $R^2 = R^3 = R^4 = Cl$



(III)

investigation. Small and his co-workers studied the reactions of this compound but were unable to obtain evidence for the position of the chlorine substituents. However, by analogy with the structure of dichlorocodide (IV), they suggested that chloro groups would be found on C 1 and C 6.

The nuclear magnetic resonance spectrum of α-chlorocodide (V) has been analysed by the present authors[2] and is reproduced with that of the trichlorocodide

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[1] Small, L., Faris, B. F., and Malonee, J. E., *J. Org. Chem.*, 1940, **5**, 334.
[2] Batterham, T. J., Bell, K. H., and Weiss, U., *Aust. J. Chem.*, 1965, **18**, 1799.

in Figure 1. The chemical shifts of most of the protons in both compounds are listed in Table 1. From these figures it can clearly be seen that the only peaks in the

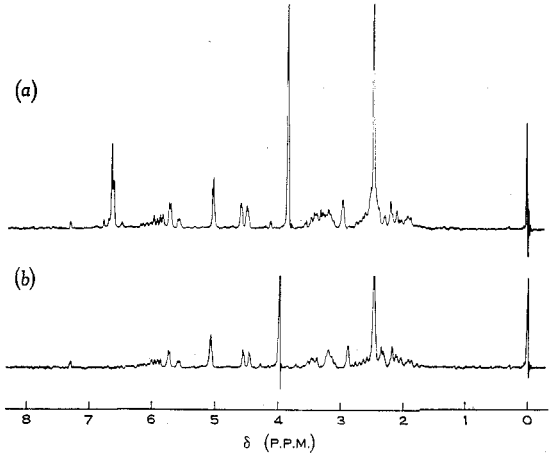

Fig. 1.—N.m.r. spectra in $CDCl_3$.
(*a*) α-Chlorocodide.
(*b*) Trichlorocodide.

spectrum of α-chlorocodide which are missing from the spectrum of the trichlorocodide are those due to the aromatic protons on C1 and C2. As the splitting patterns in these spectra are specific for isocodeine derivatives[2] the above observation unequivocally establishes structure (VI), with chlorine substituents on C1, C2, and C6, for the trichlorocodide and hence structure (VII) for the trichloromorphide.

TABLE I

COMPARISON OF CHEMICAL SHIFTS (δ) OF PROTONS OF α-CHLOROCODIDE AND TRICHLOROCODIDE

Compound	ν_1	ν_2	ν_5	ν_6	ν_7	ν_8	ν_{14}	ν_9	$\nu_{10\beta}$	OMe	*N*-Me
α-Chlorocodide	6·62	6·68	5·04	4·45	5·98	5·68	3·18	3·41	3·07	3·83	2·46
Trichlorocodide	—	—	5·06	4·42	5·98	5·70	3·16	3·44	2·96	3·98	2·46

Experimental

Spectra were run at 60 Mc/s on a hybrid HR60/A60 spectrometer of 20% solutions in deuterochloroform with tetramethylsilane (δ = 0) as internal reference.