

consumption had ceased (69 ml or 4 molar equivalents) the catalyst was filtered off and the solution kept at room temperature overnight. The crystals of sambubiose, thus obtained (0.1 g) showed: m.p. 202–203° and $[\alpha]_{578}^{27} +32^\circ$ (5 min) $\rightarrow +17^\circ$ (48 h) (c 1.0 water). (Found: C 42.31; H 6.54; C₁₁ H₂₀ O₁₀ requires: C 42.30; H 6.47).

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Nuclear Quadrupole Relaxation of ⁸⁵Rb in an Aqueous Solution of a Humic Acid

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The ion-exchange properties of humic acids are of agronomic importance as well as of theoretical interest. The total possible exchange capacity can be experimentally determined by potentiometric titrations between two arbitrarily selected pH values but it would be of great interest to have a more direct method to study the

actual attachment of the metal ions to the humic acid molecules. It seemed possible that the study of the nuclear relaxation of ⁸⁵Rb in humic acid solutions would offer such a possibility. In the present paper results are reported which show that the method actually is very promising.

The principles of the method used have been described in a number of papers.¹ The present measurements were made at $28 \pm 1^\circ\text{C}$ on a Varian V-4200 NMR spectrometer. For experimental details, see Ref. 2. The humic acid was obtained by pyrophosphate extraction at pH 7 from a peat soil. The fractionation and the soil has been described elsewhere.³ The humic acid was precipitated in acid solution and dissolved by RbOH in a solution containing 0.5 M RbCl.

For rubidium ions which are free to move in an aqueous solution of 0.5 M RbCl the line width of the ⁸⁵Rb magnetic resonance signal is 0.24 gauss (Fig. 1a). When the same measurements are carried out in a neutral humic acid solution, containing 5 g humic acid/l solution an appreciable line-

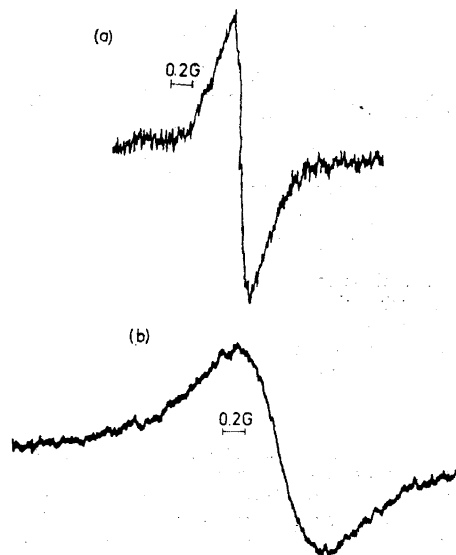


Fig. 1. The ⁸⁵Rb nuclear magnetic resonance signals (the figure shows the derivatives of the absorption signals) from (a) a 0.5 M RbCl solution and (b) a 0.5 M RbCl solution to which have been added 5 g humic acid/l solution and a small amount of RbOH in order to dissolve the acid. The spectra were recorded at a magnetic field strength of 14.0 kG.

broadening effect is observed, the line width being 0.9 gauss (Fig. 1b). The bonding of the cation to the polyelectrolyte anion can thus be directly studied.

Detailed studies of different humic acids, more or less fractionated by common methods, have been initiated and the results will be reported later.

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Note on the Optical Resolution of α -(3-Nitrophenoxy)-propionic Acid

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The resolution of the three α -nitrophenoxy-propionic acids has been described by Fourneau and Sandulesco,¹ but they found no method for isolating the (+)-form of the 3-nitrophenoxy acid. In connection with work on steric effects in synthetic growth regulators,² we needed both forms of the acid: various substituted phenoxy-propionic acids can be obtained from the nitro derivatives *via* reduction and diazonium reactions.

Experimental. Laevorotatory acid was prepared *via* the strychnine salt.¹ From the mother liquors after this salt, an acid having $[\alpha]_D^{25}$ about $+20^\circ$ was isolated. This acid (24.7 g, 0.117 mole) was dissolved with 15.8 g (0.117 mole) (+)- β -phenyl-isopropylamine in 45 ml ethanol + 100 ml water. The salt was recrystallised to constant activity of the acid (measured in absolute ethanol on samples isolated from the successive salt fractions; see Table 1).

The acid was isolated in the conventional way and recrystallised three times from carbon tetrachloride (once with charcoal). It formed pale yellow needles with m.p. $100-101^\circ$. 0.2210 g in 10.00 ml abs. ethanol: $\alpha_D^{25} = +2.283^\circ$ (2 dm). $[\alpha]_D^{25} = +51.65^\circ$. The rotation was practically unchanged when the same solution was investigated at 20°C .

The (-)-form isolated according to Ref. 1 was quite similar to the (+)-form. M.p. $100-$

Table 1.

Crystallisation	1	2	3	4	5
ml ethanol	45	25	25	20	15
ml water	100	60	50	50	40
g salt obtained	26.5	24.5	22.5	20.7	19.7
$[\alpha]_D^{25}$ of the acid	$+45.5^\circ$	$+48.5^\circ$	$+50^\circ$	$+50^\circ$	$+50^\circ$

Preliminary experiments with conventional bases gave negative results, but the acid could be resolved with optically active β -phenyl-isopropylamine (benzedrine). The first crystallisation of the salt from dilute ethanol gives an acid containing about 45% of active form with the same direction of rotation as the amine used. Maximum activity is easily obtained by recrystallisation of the salt. For practical purposes it may, however, be most convenient to isolate the (-)-form *via* the strychnine salt as described by Fourneau and Sandulesco.¹

101° . 0.2202 g in 10.00 ml abs. ethanol: $\alpha_D^{25} = -2.276^\circ$ (2 dm). $[\alpha]_D^{25} = -51.68^\circ$.

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