

pyrrolidine diester II, b.p. 83°–85°/0.5 mm, n_D^{25} 1.4589, *I.R.* (CHCl_3) 3.0, 5.8, and 11.3 μ (found: C, 57.90; H, 7.64; N, 6.41. $\text{C}_{11}\text{H}_{17}\text{O}_4\text{N}$ requires C, 58.13; H, 7.54; N, 6.16 per cent). This product by alkaline hydrolysis and subsequent decarboxylation in 10⁻⁴ M hydrochloric acid gave, in 65 per cent yield, the hydrochloride of I, which crystallized from ethanol-ethyl acetate in fine plates, m.p. 217°–218° decomp., *I.R.* ('Nujol') 11.3 μ (found: C, 44.03; H, 6.13; N, 8.36; Cl, 21.43. $\text{C}_6\text{H}_{10}\text{O}_2\text{NCl}$ requires C, 44.05; H, 6.16; N, 8.56; Cl, 21.67 per cent). Isolation of the free amino-acid was accomplished by treatment of the hydrochloride with a slight excess of silver carbonate. The resulting 4-methylene-DL-proline (I) crystallized from wet methanol-ethyl acetate in 85 per cent yield as fine, matted needles, m.p. 243°–245° decomp. (capillary, rapid heating). *I.R.* ('Nujol' or potassium bromide) $\text{C}=\text{CH}_2$ at 11.3 μ , nuclear magnetic resonance (D_2O , acetone reference) $\text{C}=\text{CH}_2$ as a close quartet centred at 4.85 τ (no methyl protons) (found: C, 56.73; H, 7.30; N, 10.87. $\text{C}_6\text{H}_9\text{O}_2\text{N}$ requires C, 56.68; H, 7.14; N, 11.02 per cent).

Through the kindness of Dr. L. Fowden, University College, London, a sample of 4-methyleneproline isolated from loquat seeds² was made available to us for comparison. In addition to having identical nuclear magnetic resonance spectra (D_2O) and indistinguishable paper chromatographic behaviour², the natural and synthetic substances had completely superposable infra-red spectra ('Nujol' and potassium bromide), identical crystallization characteristics, and undepressed mixed melting point (242°–245° decomp.), and also gave a common product on catalytic hydrogenation (mainly *cis*-4-methyl-DL-proline^{1,2}, m.p. 233°–235° decomp.), thereby directly confirming not only the structure but also the racemic character of the natural amino-acid.

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ALBERT W. BURGSTAHLER
MICHAEL L. TROLLOPE
CHARLES E. AIMAN

Department of Chemistry,
University of Kansas,
Lawrence.

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Electron Spin Resonance Spectrum of Irradiated Cellulose II

AN asymmetric electron spin resonance spectrum has usually been reported for the free radicals produced by the γ -irradiation of cellulose^{1,2}. During the course of an investigation on the effect of crystallinity and cross-linking on the degradation of cellulose by γ -radiation we noticed that while specimens of ramie and cotton (cellulose I) gave the familiar asymmetric electron spin resonance spectrum (Fig. 1B), all the samples of regenerated cellulose (cellulose II) gave the more symmetric pattern (Fig. 1A).

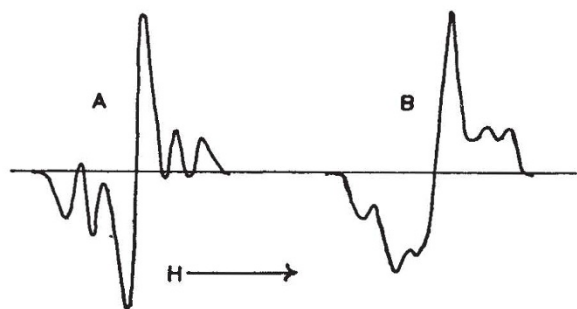


Fig. 1. Differential plot of the electron spin resonance spectra of cellulose specimens several weeks after receiving a 10-megarad dose of γ -radiation. H, Increasing field; A, regenerated cellulose; B, cotton

While the cause of this difference has not been further investigated, its relationship to the differences in the X-ray fibre diagram³ is of interest. We have recently shown from the relationship between the radical concentration and the degree of crystallinity that the stable radicals in cellulose are in the ordered regions. It follows that the differences in electron spin resonance pattern reported here must be a reflexion of the differences in molecular arrangement in cellulose I and cellulose II crystallites and might be expected to yield further information about these structures.

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G. S. PARK

Department of Chemistry,
Welsh College of Advanced Technology,
Cardiff.

J. C. WARD

C.S.I.R.O.
Division of Coal Research,
P.O. Box 175,
Chatswood,
New South Wales, Australia.

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Crystal and Molecular Structure of Glaucarubin

GLAUCARUBIN, a bitter lactone found in *Simaruba glauca*, and used medicinally as an amoebicide, has the empirical formula $\text{C}_{25}\text{H}_{36}\text{O}_{10}$ and a molecular weight of 496. Its chemical structure is known to be similar to that of chaparrin² and quassin³. Recently the chemistry of the family Simaroubaceae has been the subject of a considerable number of investigations^{4,5}. Examination of the structure of this compound had been in progress in the Department of Medicinal Chemistry, State University of New York at Buffalo, when it was decided to apply X-ray crystallographic methods to this problem. The crystals of *p*-bromobenzoate derivative were prepared at this department and the X-ray investigations were undertaken at the Roswell Park Memorial Institute at Buffalo, with the hope that a complete single crystal structural study of this compound would contribute useful information about the chemistry of this class of compounds.

The crystal structure of *p*-bromobenzoate derivative has now been solved from three-dimensional X-ray diffraction data collected on a General Electric XRD 5 single crystal diffractometer equipped with a goniostat. It was found that this compound crystallizes in the monoclinic system and belongs to the space group $P2_1$. The cell contains two molecules and has dimensions as follows:

$$a = 13.79 \text{ \AA} \quad b = 6.99 \text{ \AA} \quad c = 17.35 \text{ \AA} \quad \beta = 110.8^\circ$$