# Constitution of Resin Phenols and their Biogenetic Relations

## XXII *. On the Absolute Configuration of Lignans

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The sterical relationships between the known members of the lignan series are largely established (for references see Erdtman [1] and Hearon and MacGregor [2]). If therefore the absolute configuration of one of the lignans could be determined this would simultaneously establish the confiration of all the interrelated lignans.

The work of Bijvoet *et al.*[3] has shown that the absolute configuration of glyceraldehyde is the same as that arbitrarily adopted by Fischer. In order to correlate the lignans with glyceraldehyde the conversion of dextrorotatory bis(hydroxymethyl)-succinic acid dilactone, obtained from pinoresinol, into compounds of known configuration has been investigated. These experiments have hitherto been unsuccessful, however, a promising route for the solution of the problem has now been found.

(−)-Dihydroguaiaretic acid dimethylether(I) afforded a weakly dextrorotatory dimethyladipic acid (II) on ozonolysis followed by oxidation with hydrogen peroxide. This acid was very readily converted into a dimethyl*cyclo*pentanone which shows a very high negative rotation. The formation of the *cyclo*pentanone demonstrates that the ozonolysis in fact has given the expected acid (II).

Work is in progress to correlate this acid with dimethylsuccinic acid (III) both by synthetic and degradative methods. By removing the carboxyl group of the half-ester of the dimethylsuccinic acid it is hoped to obtain α-methylbutyric acid (IV) which has already been correlated with glyceraldehyde (*cf.* Crombie and Harper [4]). The details of these correlation experiments and a discussion of the results will be published shortly.

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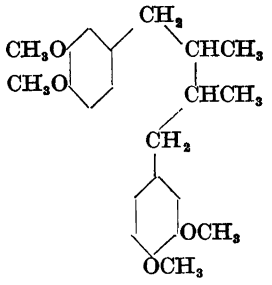
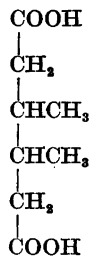
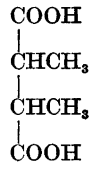
2. Hearon, W. M. and MacGregor, W. S. *Chem. Rev.* **55** (1955) 957.



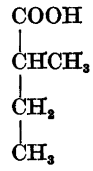
I



II



III



IV

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# Optical Resolution of α-Phenylglutaric Acid

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In connection with current work on steric relationships, the authors have resolved α-phenylglutaric acid into its

optical antipodes. Quinine in ethanol and brucine in methanol were found to give the best results.

The racemic acid, prepared through the anhydride [1], had the m.p. 100–102°. The value 82–83° reported by previous authors [2] obviously refers to an unstable modification. The optically active acid melted at 129–131°.

*Experimental.* The anhydride was prepared by conventional methods [1]. After distillation *in vacuo* and recrystallisation from ethyl acetate + hexane, it melted at 94–95°. It was hydrolysed with boiling water (30 minutes); after extraction with ether and evaporation of the solvent, the acid was obtained as a gradually crystallising syrup. After recrystallisation from formic acid, it melted at 98–101°; further recrystallisation from ether + petrol ether raised the m.p. to 100–102°.

**33.5 g racemic acid and 104 g quinine were dissolved together in 800 ml 96-% ethanol. The salt obtained after standing over-night was recrystallised seven times from the same solvent. The activity of the acid was practically constant from the fourth recrystallisation. The salt obtained (32.8 g) was decomposed with dilute sulphuric acid and the phenylglutaric acid isolated by extraction with ether. M. p. 129–131°. (Found: equiv.wt 104.7. $C_{11}H_{12}O_4$ requires 104.1. $[\alpha]_D^{25} = +85.8°$, $[M]_D^{25} = +178.5°$ in ethanol solution.)**

The mother liquor from the first crystallisation of the quinine salt was evaporated and the acid liberated. 13.7 g with $[\alpha]_D^{25} = -46.8°$ was obtained. It was dissolved with 62 g brucine in 150 ml methanol. The salt obtained after 24 hours was recrystallised seven times from the same solvent; after five recrystallisations, the activity of the acid was constant and had practically the same maximum value as the antipode. The yield of salt was 27.9 g.

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# Synthesis of Racemic Methyl Phthienoate

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In the lipids of a human strain of the tubercle bacillus Anderson and Chargaff in 1929 [1,2] found a dextrorotatory, branched chain fatty acid which they called phthioic acid. When injected into animals, this acid was found [3] to produce epitheloid cell tissue reaction characteristic of tuberculosis. The elucidation of the chemical structure of the compound proved difficult and has been achieved only recently, mainly as a result of work by Polgar *et al.*[4–6] at Oxford and by Cason *et al.*[7–9] at Berkeley. After the $\alpha,\beta$-unsaturation of the acid had been recognized [4,7] the new names mycolipenic acid-I[b] and $C_{27}$-phthienoic acid [8] were suggested. According to Cason and Sumrell [8] several homologues of $C_{27}$-phthienoic acid are present in the lipids of tubercle bacilli.

On the basis of the above-mentioned degradation studies at Oxford and Berkeley, and synthetic work performed at Uppsala, Ställberg-Stenhagen [10] suggested that $C_{27}$-phthienoic acid ** is *trans*-2,4L, 6L-trimethyl-$\Delta^{2:3}$-tetracosenoic acid. This conclusion has been strengthened by Fray and Polgar's recent synthesis [11] of (+)-2L,4L-dimethyldocosanoic acid, a degradation product of the natural compound. The synthesis of the *cis*- and *trans*-DL-erythro isomers of methyl 2,4,6-trimethyl-$\Delta^{2:3}$-tetracosenoate has now been performed through the following sequence of reactions:

* Rockefeller Foundation fellow.

** We prefer this name because of its similarity with the name originally proposed by R. J. Anderson.