

The Occurrence of D-(+)-Allose in Nature

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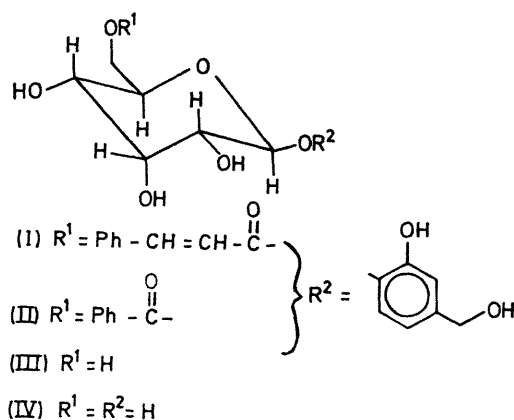
Summary D-(+)-Allose has been obtained in pure form from leaves of *Protea rubropilosa*, in which it is present as the 6-*O*-cinnamate (rubropilosin) and as the 6-*O*-benzoate (pilorubrosin) of 2'-hydroxy-4'-hydroxymethyl-phenyl β -D-allopyranoside.

ONLY four of the eight D-aldohexoses have so far been found in Nature, *viz.* D-glucose, D-galactose, D-mannose, and D-talose; an allose of undetermined configuration has been shown to occur in a fresh-water algae.¹

We report that the leaves of *Protea rubropilosa* Beard (fam. Proteaceae), collected on Mariepskop, Eastern Transvaal, where the plant grows as a tree-like bush about 3 m in height, contain two ester glycosides, rubropilosin (I) and pilorubrosin (II), as major components. These are the 6-*O*-cinnamate and -benzoate respectively of the 2'-hydroxy-4'-hydroxymethyl-phenyl β -glycoside (III) of the pyranose form of D-(+)-allose (IV).

Rubropilosin (I), needles from aqueous ethanol, C₂₂H₂₄O₉, obtained in 0.59% yield from the dried leaves by chromatography of the methanol extract and crystallisation, had m.p. 97–100°, $[\alpha]_D -69^\circ$ (*c.* 1 in 96% ethanol). Pilorubrosin (II), needles from water, C₂₀H₂₂O₉, obtained in 0.47% yield as above, had m.p. 167–169°, $[\alpha]_D -66^\circ$ (*c.* 0.87 in methanol). Hydrolysis with hot aqueous barium hydroxide solution yielded cinnamic acid from (I), and benzoic acid from (II), as well as the deacylated glycoside (III). Catalytic hydrogenolysis of (III) (Pd/C) followed by acid hydrolysis gave 3,4-dihydroxytoluene and D-(+)-allose (β -pyranose form) which, after purification *via* its pentaacetate, had m.p. 130–132° (from methanol) (lit., 128–128.5°² and 130–131°³); $[\alpha]_D^{20} +14.5 \pm 0.3^\circ$ (equilibrium; *c.* 1.1 in water) (lit.,² +14.4°, *c.* 1.3 in water); an undepressed mixed m.p., and identical i.r. spectra (in KBr dispersion), were obtained⁴ with synthetic D-(+)-allose (m.p. 129–132°) obtained from D-(–)-ribose, as well as with an authentic sample; the ratio of the g.l.c. retention time of the trimethylsilyl ether relative to that of α -glucose was 0.80 on a GE SE-52 column (carrier gas He) at 180° (lit.,⁵ 0.81 at 140°), and no peak splitting was found on mixed injection with the

authentic D-(+)-allose derivative at 200°, 190°, and 180°. The *p*-bromophenylhydrazone had m.p. 144–147° (lit.,⁶ 145–147°) and the phenylsazone had m.p. 162–163° (lit.,³ 162–163°, decomp.), both derivatives being identical (by mixed m.p. and i.r. spectra) with samples prepared from authentic D-(+)-allose.



The pyranose form of the D-(+)-allose moiety was demonstrated by analysis of the mass spectrum of the hexa-acetate,⁷ prepared from (III) under basic conditions, while the configuration of C-1 and the positions of substitution of R¹ and R² were deduced from spectral analysis and from the chemical behaviour⁸ of the tri-*O*-methyl derivative of (IV) obtained from per-*O*-methylated (I) and (II). The full details are being submitted for publication elsewhere and include formal proof for the pyranose structure of the isolated β -(D)-(+)–allose.

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