Summary

The series of 2-methyl and 2-ethyl-4-(*p*-halogenated phenyl) thiazoles has been completed by preparation of the fluorine analogs.

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Emil Fischer's Assignment of Configuration to *d*-Glucose. The Pentaacetates of *d*-Arabitol and *d*-Xylitol[1]

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To decide between two alternative configurations for *d*-glucose, Fischer investigated the trihydroxyglutaric acids derived from *l*-arabinose and *d*-xylose[2] and found the former to show $[\alpha]^{20}_{\mathrm{D}}$ −22.7° in water, while the latter was inactive and must therefore contain the symmetrical configuration. Theoretically, the same conclusions could have been drawn from the properties of the corresponding pentitols which must contain the same symmetries, respectively, as the acids, and it is therefore remarkable to note that, in 1891, the literature recorded *l*-arabitol as optically inactive[3] and *d*-xylitol as active,[4] or just the opposite situation to that obtaining with the acids. Fischer resolved the anomaly by augmenting the rotation of arabitol just to the visible with borax, and satisfied himself as to the inactivity of xylitol by partially purifying the sirupy alcohol by its conversion to dibenzalxylitol, which, however, proved to be too insoluble to recrystallize.

The true optical nature of these pentitols can, however, be shown very readily and quite conclusively by converting them to the corresponding acetates, which are formed in quantitative yields, crystallize well and can easily be purified. The rotation of the active isomer (*d*-arabitol) is thus augmented to an easily read value of $[\alpha]^{20}_{\mathrm{D}}$ in $CHCl_3$ + 37.2°, while the acetate of the inactive xylitol remains inactive. Thus any possibility that xylitol could be inactive through *fortuitous* internal compensation without a true plane of symmetry is removed. (*Cf.* β-methyl-*d*-galactoside, which is asymmetric yet nearly inactive. Its acetate shows $[\alpha]^{20}_{\mathrm{D}}$ in $CHCl_3$ −13°, however.)

We believe that this method of proof is pedagogically superior to that of Fischer, based upon the properties of the acids, since the yields are more nearly quantitative and the rotation of the active isomer actually greater. The necessary reactions could readily be carried out by advanced students as part of a laboratory exercise to prove the configuration of *d*-glucose. The pentitols were acetylated by warming with four parts of acetic anhydride and one-quarter part of fused sodium acetate.

d-Arabitol pentaacetate separates from water–methanol mixtures as large, clear, tabular prisms, m. p. 74–75° (corr.) and $[\alpha]^{20}_{\mathrm{D}}$ in $CHCl_3$ + 37.2° (*c*, 7.31; 4-dm. tube). *d*-Xylitol pentaacetate crystallizes from water–methanol mixtures as large, clear, tabular prisms which melt at 61.5–62.5° (corr.) and are wholly inactive (*c*, 1.61 in $CHCl_3$; 2-dm. tube).

Several investigators[5] have recently isolated *d*-arabitol from lichens. Several of them also prepared the acetate and found it to melt at 75° but did not record the rotation. Dr. Asahina informs us that a sample of authentic *d*-arabitol pentaacetate which we sent him gives an undepressed m. p. of 76° when mixed with the pentaacetate of his natural pentitol.

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[2] Fischer, *Ber.*, **24**, 1836, 2683 (1891).

[3] Kiliani, *ibid.*, **20**, 1234 (1887).

[4] Bertrand, *Bull. soc. chim.*, **5**, 556 (1891).

[5] Nolan and Keane, *Nature*, **132**, 281 (1933); Yabuta and Sumiki, *J. Agr. Chem. Soc. Japan*, **9**, 492 (1933); Asahina and Yanagita *Ber.*, **67**, 799 (1934); Klima, *Monatsh.*, **62**, 209 (1933).