A Relationship between Optical Activity and Glucose Content of Hydrolysable Tannins

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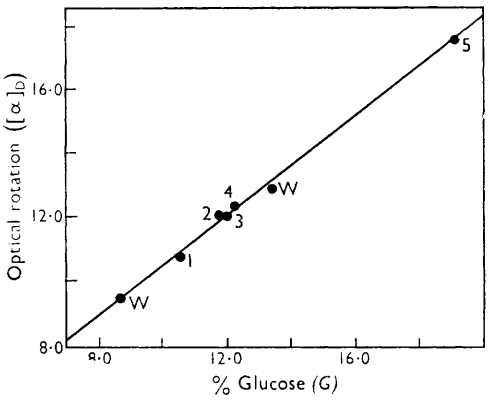
HYDROLYSABLE tannins of known structure consist of a polyhydric aliphatic alcohol esterified with gallic acid or derivatives of gallic acid. The work of Haworth[1] and his co-workers has shown that a subdivision of the gallotannins can be made on the basis of the esterified alcoholic core present, for example, Chinese, Sicilian summach, and Stagshorn summach tannins[2] have a penta-*O*-galloyl-β-D-glucose core further esterified with gallic acid, whereas Turkish tannin[3] has a mixture of **3,4,6-** and **2,3,6-**tri-*O*-galloylglucoses as its core, and Tara tannin[4] has a core of **3,4,5-**tri-*O*-galloylquinic acid.

In connection with investigations of the tannins in leaves of various plant species[5] it was desirable to establish a quick general method for identification of the core of hydrolysable tannins. To this end we have correlated the optical rotations

[1] R. D. Haworth, *Proc. Chem. Soc.*, 1961, 401.
[2] R. Armitage, G. S. Bayliss, J. W. Gramshaw, E. Haslam, R. D. Haworth, K. Jones, H. J. Rogers, and T. Searle, *J.*, 1961, 1842.
[3] R. Armitage, E. Haslam, R. D. Haworth, and T. Searle, *J.*, 1962, 3808.
[4] E. Haslam, R. D. Haworth, and P. C. Keen, *J.*, 1962, 3814.
[5] B. R. Brown, C. W. Love, and W. R. C. Handley, *Rep. Forest Research*, 1962, 90.

of known galloylglucoses and tannins with their glucose contents. A plot of the specific rotation ($[\alpha]_D$) for acetone solutions of a series of penta-*O*-galloyl-β-D-glucoses against the weight per cent of glucose (*G*) gives a good straight line (see Figure), the equation to which is:

$$[\alpha]_D = 0{\cdot}76G + 2{\cdot}9 \qquad (1)$$



Relationship between specific rotation and glucose content for penta-O-galloyl-β-D-glucoses: 1, *penta*-O-(m-*digalloyl*)-β-D-*glucose*,[6] 2 *Stagshorn summach tannin*,[2] 3 *Chinese tannin*,[2] 4 *Sicilian summach tannin*,[2] 5 *penta*-O-*galloyl*-β-D-*glucose*,[2] *W fractions of willow herb tannin.*

[6] E. Fischer, and M. Bergmann, *Ber.*, 1919, **52**, 829.

The recorded data for Turkish tannin[3] and tara tannin[4] are widely different and fall well clear of the penta-*O*-galloyl-β-D-glucose line. However, it is interesting to note that the values for the three fractions of different molecular weight into which Haworth *et al.* separated Turkish tannin,[3] fall on a different straight line whose equation is:

$$[\alpha]_D = 3{\cdot}6G - 36 \qquad (2)$$

Since the core of this tannin consists of a mixture of trigalloylglucoses, it is not possible to use synthetic compounds to substantiate this particular relationship further. It is not surprising that general relationships of this kind are found since, given a constant core, further galloyl substitution occurs at points sufficiently remote from the asymmetric centres of the glucose residue for one to expect the molecular rotation of this residue to be unaffected.

We have found the relationship useful in assigning a penta-*O*-galloyl-β-D-glucose core to two tannin fractions which we have isolated from leaves of willow herb (*Chamaenerion angustifolium*), since the values of $[\alpha]_D$ and *G* for these fractions fall on the line for the pentagalloylglucose compounds (see Figure).

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