The Absolute and Relative Stereochemical Correlation of Isoflavanone, Sophorol and Naturally-occurring Isoflavan Derivatives

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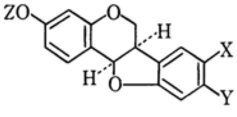
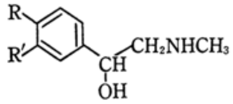
The absolute and relative stereochemical correlations between corresponding asymmetric centers of optically acitve isoflavanone, sophorol[1] and various chromanocoumarans, including (−) homopterocarpin[2a] (I) X=H, Y=OMe, Z=Me, (−) maackiain[2b] (I) X and Y=methylenedioxy, Z=H and (−) trifolirhizin[11,2c] (I) X and Y=methylenedioxy, Z=-D-glucose, have not yet been defined.

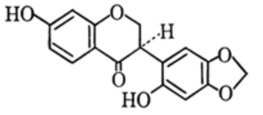


(I)

The optical rotatory-dispersion curves of sophorol, the oxidation product of *O*-methyldihydropterocarpin[3] and *O*-dimethylsophorol, exhibit virtually identical plain positive dispersion curves throughout the spectral range under examination. This result can be taken as conclusive evidence of an identical absolute configuration at C^3 in sophorol and the corresponding asymmetric center[4] of maackiain and the related compounds; it thus confirms previous assumptions.[5] The rotatory-dispersion curves of homopterocarpin, pterocarpin and maackiain all exhibit negative cotton effect curves. In these cases C^3 asymmetric carbon in the chromanocoumaran molecule makes a very weak negative contribution,[6] as is shown in the dispersion curve of dihydro-*O*-methylmaackiain *O*-methylether. Therefore, the relatively strong negative rotation accompanying by the cotton effects in these compounds is probably produced by the C^4 asymmetric center.

Lyle[7] reported that the compounds of the II, III, IV, (I) ephedrine and (−)-ψ-ephedrine types showed negative cotton effects of a similar shape, and he identified the absolute configuration of (−) halostachine (II) as R on the basis of an unequivocal chemical correlation.[7]





(II) R=R′=H
(III) R=H, R′=OH
(IV) R=R′=OH

(V)

Attention must be drawn to the structural similarity between the asymmetric center of halostachine (II) and the environment of the corresponding asymmetric center of pterocarpin. Although, in the series of compounds in the present case, the aromatic ring is not free to rotate, and the enhancement of the optical activity can be observed,[8] the negative cotton effects by the asymmetric center of the R configuration in halostachine (II) and the C^4 environment of pterocarpin are strong evidence for assuming that the asymmetric centers of these compounds have the same absolute configuration R.

Since the B/C ring junction in pterocarpin is cis,[9] pterocarpin is represented as the C^4R, C^3R, configuration (I). Consequently, all the other chromanocoumarans which have been reported to exhibit negative rotation can be identified as having the C^4R, C^3R, configuration. Since it is apparent from the O. R. D. curve that C^3 in the isoflavan equol[10] and the corresponding asymmetric center of dihydro *O*-methylmaackiain-*O*-methylether have the same absolute configuration, the C^3 center of equol is assigned the R configuration. Therefore, sophojaponicin[11] must have the C^4S, C^3S configuration.

Furthermore, it follows that the absolute configuration of C^3 of sophorol is R (V). The present assignment of the absolute configuration should, however, be examined by an unequivocal chemical correlation.*

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[1] a) H. Suginome, *J. Org. Chem.*, **24**, 1655 (1959); *Tetrahedron Letters*, **1960** 16.

[2] a) E. Späth and J. Schläger, *Ber.*, **73**, 1 (1940). b) H. Suginome, *Experientia*, **18**, 161 (1962). c) J. B. Bredenberg and P. K. Hietala, *Acta. Chem. Scand.*, **936**, 15 (1961); Y. Fujise, T. Toda and S. Ito, *Chem. Pharm. Bull. Japan*, **11**, 167 (1963).

[3] A. McGookin, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, **1940** 787.

[4] The numbering system of chromanocoumaran was chosen arbitrarily since it is an isoflavone derivative.

[5] W. B. Whally, "The Chemistry of Flavonoid Compounds," T. A. Geissman ed., Pergamon Press London (1962), p. 441.

[6] The formation of ring compounds from open chains is accompanied by an increase in the optical rotation.[8]

[7] G. G. Lyle, *J. Org. Chem.*, **25**, 1779 (1960).

[8] W. J. Kauzmann, J. E. Walter and H. Eyring, *Chem. Revs.*, **26**, 339 (1940).

[9] H. Suginome and T. Iwadare, *Experientia*, **18**, 163 (1962).

[10] G. F. Marrian and D. Beall, *Biochem. J.*, **29**, 1586 (1935).

[11] S. Shibata and Y. Nishikawa, *Chem. & Pharm. Bull.*, **11**, 167 (1963).

* After this paper was prepared, Professor S. Ito informed us that he and his colleagues had assigned C^4R, C^3R as the absolute configuration of trifolirhizin on the basis of the chemical correlation.