

TABLE 1. ^{13}C chemical shifts of inositols.

| Inositol | Carbon no.* | Equation† | δ_{CS_2} (ppm) | δ_{calc} |
|---------------|-------------|-------------------|------------------------------|------------------------|
| <i>scyllo</i> | 1-6 | — | 118.2 | (118.2) |
| <i>myo</i> | 1, 3 | β | 119.5 | 119.9 |
| | 2 | — | 119.7 | (119.7) |
| | 4, 6 | γ | 120.8 | 121.0 |
| <i>chiro</i> | 5 | δ | 117.6 | 117.5 |
| | 1, 6 | β' | 120.3 | 120.3 |
| | 2, 5 | $\beta + \gamma$ | 121.4 | 122.7 |
| | 3, 4 | $\gamma + \delta$ | 119.1 | 120.3 |
| <i>epi</i> | 1, 5 | $\beta + \delta$ | 120.2 | 119.2 |
| | 2, 4 | λ' | 117.4 | 117.4 |
| | 3 | 2β | 121.8 | 121.6 |
| | 6 | 2γ | 125.1 | 123.8 |

* Carbons are numbered as in 1-4.

† Not including references values of 118.2 or 119.9 ppm as appropriate.

The data in Table 1 permit derivation of a set of empirical constants which can be used to correlate and predict the spectra of the inositols as well as many of those carbohydrates which occur with pyranose rings.^{2, 5} For carbons carrying a single equatorial hydroxyl group and surrounded by carbons all with equatorial hydroxyls, the position (118.2 ppm) of the single carbon resonance of *scyllo*-inositol (1) provides an obvious reference point. Changes in chemical shift will be expected with changes in the configurations of the hydroxyls in the molecules while the hydroxyl on the carbon under consideration is kept in the equatorial position. In the ensuing discussion, we will let β represent the shift in ppm caused by a change in hydroxyl configuration on the immediately adjacent carbon,⁶ while γ and δ will represent the shifts associated with changes in configuration of hydroxyls on γ and δ carbons, respectively. On this basis, the C-1 resonance of *epi*-inositol (4) will be expected to be observed at $\beta + \delta$ ppm relative to the carbon resonance of *scyllo*-inositol (1).

For carbons having an axial hydroxyl group, another reference point is required and we will use the C-2 resonance (119.7 ppm) of *myo*-inositol (2) for this purpose. The changes in shift connected with changes of configuration of other hydroxyls in the molecule will be designated as β' , γ' , and δ' . The shift of the C-2 resonance of *epi*-inositol (4) will then be γ' .

Best values for the constants β , β' , γ , etc., obtained by the method of least squares in ppm are as follows: $\beta = 1.7 \pm 0.3$, $\gamma = 2.8 \pm 0.3$, $\delta = -0.7 \pm 0.5$, $\beta' = +0.6$,⁸ and $\gamma' = -2.3$.⁸

Unfortunately, *neo*-inositol (5) was not sufficiently soluble to permit a determination of δ' . The chemical shifts calculated for the inositol carbon resonances are compared with the experimental values in Table 1. The agreement corresponds to a linear correlation coefficient of 0.93 with a standard deviation of 0.8 ppm. This is not itself an especially impressive achievement in that it involves the fitting of a five-parameter equation to ten independent chemical shifts. Nonetheless, the parameters so obtained have proved very useful in correlating the carbon chemical shifts of monosaccharides.²

The pattern of the parameters β , γ , etc., generally conforms to the idea that steric hindrance or proximity effects are especially important. Thus γ and γ'

have the largest numerical values, as befits 1,3-diaxial interactions in these systems,^{5, 7, 9, 10} while δ , the long-range parameter, is small.

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† National Institutes of Health postdoctoral fellow, 1967-1969.

¹ Weigert, F. J., M. Jautelat, and J. D. Roberts, these PROCEEDINGS, 60, 1152 (1968).

² Dorman, D. E., and J. D. Roberts, manuscript in preparation.

³ Grant, D. M., and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).

⁴ Weigert, F. J., and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 2967 (1967).

⁵ Similar treatments of the ¹³C spectra of alkylcyclohexanes have been made by D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967).

⁶ The designation of this change as occurring at a "β-carbon" is in accord with correlations of chemical shifts in other systems.^{5, 7}

⁷ Roberts, J. D., F. J. Weigert, J. Kroschwitz, and H. J. Reich, manuscript in preparation on ¹³C chemical shifts of acyclic and alicyclic alcohols.

⁸ Insufficient examples were available to provide estimates of reliability for these values.

⁹ Angyal, S. J., and D. J. McHugh, *Chem. Ind. London* (1956), p. 1147.

¹⁰ Similar effects are of paramount importance in determining ¹³C chemical shifts in steroids (Reich, H. J., M. Jautelat, and J. D. Roberts, manuscript in preparation).