

The Absolute Configuration of Dimorphecolic, Lesquerolic, and Densipolic Acids

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WE have been interested¹ in the absolute configurations of the naturally occurring hydroxy-acids, dimorphecolic² (I) (9-hydroxy-*trans,trans*-10,12-octadecadienoic), lesquerolic³ (II) (14-hydroxy-*cis*-11-eicosenoic), and densipolic⁴ (III) (12-hydroxy-*cis,cis*-9,15-octadecadienoic) since their initial discovery by Smith and his co-workers.²⁻⁴ Optical rotatory dispersion (o.r.d.) measurements coupled with the earlier work of Serck-Hanssen⁵ and the recent studies of Schroefer and Bloch⁶ now permit us to assign absolute configurations to these unsaturated hydroxy-acids.

Highly purified samples of the methyl esters of the unsaturated acids⁷ (I—III) and their saturated derivatives, together with ricinoleic acid (IV) (12-hydroxy-*cis*-9-octadecenoic acid) and its reduced product, were examined from 600 μ to

about 250 μ in methanol solutions with a Cary 60 spectropolarimeter. Calibration and operation have been described elsewhere.⁸ All of the saturated derivatives have plain negative curves, strongly suggesting that these acids are of the D-configuration. The result is, of course, unequivocal in the case of the 12-hydroxyoctadecanoic and 9-hydroxyoctadecanoic compounds, for they have been shown previously to be of the D-configuration.^{5,6} Since no inversion occurs on catalytic hydrogenation, the corresponding unsaturated acids are also of the D-configuration. For the methyl esters of the saturated derivatives of (I—IV), typical values are: (I) $[\alpha]_{589} - 0.17$, $[\alpha]_{250} - 1.24$; (II), $[\alpha]_{589} - 0.23$, $[\alpha]_{250} - 1.76$; (III and IV), $[\alpha]_{589} - 0.35$, $[\alpha]_{250} - 2.09$.

In the case of the unsaturated acids (I—IV),

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¹ T. H. Applewhite, *J. Amer. Oil. Chemists' Soc.*, 1965, **42**, 321.

² C. R. Smith, Jr., T. L. Wilson, E. H. Melvin, and I. A. Wolff, *J. Amer. Chem. Soc.*, 1960, **82**, 1417.

³ C. R. Smith, Jr., T. L. Wilson, T. K. Miwa, H. Zobel, R. L. Lohmar, and I. A. Wolff, *J. Org. Chem.*, 1961, **26**, 2903.

⁴ C. R. Smith, Jr., T. L. Wilson, R. B. Bates, and C. R. Scholfield, *J. Org. Chem.*, 1962, **27**, 3112.

⁵ K. Serck-Hanssen, *Chem. and Ind.*, 1958, 1554.

⁶ G. J. Schroefer, Jr., and K. Bloch, *J. Biol. Chem.*, 1965, **240**, 54.

⁷ R. G. Binder, L. A. Goldblatt, and T. H. Applewhite, *J. Org. Chem.*, in press.

⁸ Y. Tomimatsu and W. Gaffield, *Biopolymers*, in press.

however, care must be exercised in interpreting the o.r.d. curves. Although the mono-unsaturated compounds (II and IV) show positive background curves, which become lævorotatory at low wavelengths, the doubly-unsaturated compounds (I and III) have plain curves. However, (I) has a positive plain curve whereas (III) has a negative plain curve.

Thus, on the basis of the unsaturated acids' curves alone, assignment of configuration could yield erroneous results. It would seem expedient always to reduce to the saturated alcohol before attempting measurements leading to assignment of absolute configuration.

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