Carbohydrate Research, 58 (1977) 209–211
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

Note

Specific rotation of α-D- and β-D-fructofuranose

ROBERT S. SHALLENBERGER, CHANG Y. LEE, TERRY E. ACREE, JOHN BARNARD,
AND MICHAEL G. LINDLEY
New York State Agricultural Experiment Station, Cornell University, Geneva, N. Y. 14456 (U. S. A.)
(Received August 5th, 1976; accepted for publication in revised form, November 12th, 1976)

It is now known, by virtue of gas–liquid chromatographic[1] (g.l.c.) and nuclear magnetic resonance (n.m.r.) studies[2,3], that mutarotated solutions of D-fructose contain three isomers present in measurable concentration. They have been identified[2,3] as β-D-fructopyranose, β-D-fructofuranose, and α-D-fructofuranose in the ratio of 6.5:2.7:1.0 respectively, in water, at about 36°.

By application of g.l.c. techniques previously described (having also previously established conditions under which trimethylsilylation does not significantly alter the tautomeric composition of an aqueous sugar solution) and also optical-rotatory techniques to the tautomeric composition of sugar solutions[4], we have now been able to calculate the probable specific rotations of the two furanose forms of D-fructose. The mole percent of the three fructose tautomers at equilibrium in water at various temperatures (thermal mutarotation[5]) was determined by g.l.c. separation of their pertrimethylsilyl ethers[6]. The optical rotation of the solutions in water (*c* 10) was also recorded. β-D-Fructopyranose was identified as that compound found (by g.l.c.) immediately upon the dissolution of crystalline D-fructose.

The compound herein described as β-D-fructofuranose is identical to that form of fructose initially liberated (and monitored by g.l.c.) upon the hydrolysis of sucrose with yeast invertase. The third isomer is presumed to be α-D-fructofuranose, in view of recent[2,3] n.m.r. data and also the finding that the molecular rotation (+120.5 in chloroform) of the isolated (by preparative g.l.c.) pertrimethylsilyl ether is in accord with that of methyl α-D-fructofuranoside. The molecular rotation of per-*O*-trimethylsilyl-β-D-fructofuranoside (−139.3) is also in accord with reported values for methyl β-D-fructofuranoside.

As the regression equations for each isomer of D-fructose (and also the observed specific rotations) versus the equilibrium temperature yielded linear correlation-coefficients greater than 0.99, the data shown in Fig. 1 were programmed for computer solution of the simultaneous equation:

$$(M_{\beta p})([\alpha]_{D,\beta p})+(M_{\beta f})([\alpha]_{D,\beta f})+(M_{\alpha f})([\alpha]_{D,\alpha f}) = [\alpha]_D$$

where M = mole percent. The equation ($Xb = y$) was solved by the method of

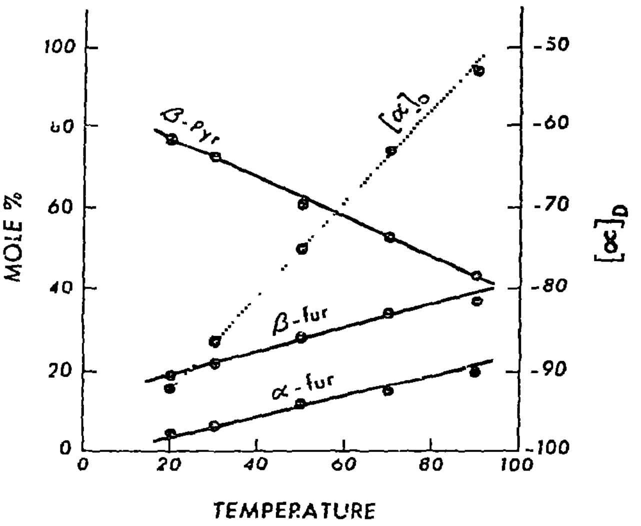

Fig. 1. The mole percent of various D-fructose tautomers, and also the specific rotation of the solutions, at different temperatures.
$\%\beta p = -0.48t + 86.72$ ($r = 0.998$)
$\%\beta f = 0.26t + 14.32$ ($r = 0.993$)
$\%\alpha f = 0.23t - 0.55$ ($r = 0.995$)
$[\alpha]_D = 0.56t - 102.6$ ($r = 0.999$).

TABLE I

SPECIFIC ROTATIONS OF β-D-FRUCTOPYRANOSE, β-D-FRUCTOFURANOSE, AND α-D-FRUCTOFURANOSE, CALCULATED FROM THE OBSERVED MOLE-PERCENT OF EACH TAUTOMER AT VARIOUS TEMPERATURES AND THE OBSERVED SPECIFIC ROTATION OF THE MIXTURE, BY MEANS OF SIMULTANEOUS EQUATIONS CONTAINING THREE UNKNOWN VALUES

Temperatures compared (degrees)	*Specific rotation (degrees)*		
	$[\alpha]_{D,\beta p}$	$[\alpha]_{D,\beta f}$	$[\alpha]_{D,\alpha f}$
20, 30, 50	−137.6	+107.6	−179.7
20, 30, 70	−140.6	+129.1	−223.6
20, 30, 90	−133.7	+80.7	−124.7
20, 50, 70	−133.2	+82.1	−141.7
20, 50, 90	−51.9	−396.2	+569.1
20, 70, 90	−124.9	+29.4	−50.1
30, 50, 70	−133.4	+86.0	−150.0
30, 50, 90	−203.1	+447.6	−653.3
30, 70, 90	−122.9	+23.4	−43.3
50, 70, 90	−131.6	+49.9	−72.8
Mean	−131 ±11	+64 ±64	−106 ±92

Gaussian elimination. The i^{th} row of the X matrix contained the observed mole-percent at the i^{th} temperature, and the i^{th} element of the vector y contained the specific rotation observed at the i^{th} temperature.

Solutions to the ten possible sets of simultaneous equations containing the three unknowns are shown in Table I. Although the standard deviation about the linear regressions as shown in Fig. 1 is experimentally acceptable, the deviation obtained, coupled with the near co-linearity of two of the parameters, leads to several "absurd" solutions to the equation and a very high standard-deviation about the mean values. Nevertheless, the average result obtained for the specific rotation of β-D-fructopyranose is in excellent agreement (±1%) with values reported in the literature[7]. Consequently, it seems to us that the mean values obtained for β-D-fructofuranose (+64°) and α-D-fructofuranose (−106°) are accurate to within ±10%.

To test the accuracy of these specific rotations, it was calculated that the specific rotation of the mutarotated solutions of D-fructose, determined by n.m.r. spectroscopy[3] to contain β-pyranose, β-furanose, and α-furanose in the ratios of 6.5:2.7:1 at 36°, should be −77° ±8°. Experimentally, we found the specific rotation at 36° to be −82.4°.

REFERENCES

1 G. G. S. Dutton, *Adv. Carbohydr. Chem. Biochem.*, 28 (1973) 11–160.
2 D. Doddrell and A. J. Allerhand, *J. Am. Chem. Soc.*, 93 (1971) 2779–2781.
3 A. S. Perlin, P. Herve du Penhoat, and H. S. Isbell, *Adv. Chem. Ser.*, 117 (1973) 39–50.
4 R. S. Shallenberger and T. E. Acree, *Carbohydr. Res.*, 1 (1966) 495–497; T. E. Acree, R. S. Shallenberger, C. Y. Lee, and J. W. Einset, *ibid.*, 10 (1969) 355–360.
5 H. S. Isbell, in F. J. Bates (Ed.), *Polarimetry, Saccharimetry and the Sugars*, Circular C 440, Natl. Bur. Stand., 1942, pp. 448–449.
6 R. Bentley and N. Botlock, *Anal. Biochem.*, 20 (1967) 312–320.
7 W. Pigman and H. S. Isbell, *Adv. Carbohydr. Chem.*, 23 (1968) 11–57.