

2-C-METHYL-D-ERYTHRITOL IN LEAVES OF *LIRIODENDRON TULIPIFERA*

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Abstract—A branched-chain alditol was isolated from yellow autumn leaves of the tulip tree, *Liriodendron tulipifera* and identified as 2-C-methyl-D-erythritol.

INTRODUCTION

2-C-methyl-D-erythritol, a compound previously unknown, was isolated from *Convolvulus glomeratus* by Anthonsen *et al.* [1] in 1976. Subsequently they synthesized its racemate [1] and later the optically active compound itself [2]. The synthesis of its enantiomer from D-apiose has also been reported [3], although the authors did not indicate which enantiomer they prepared, nor have given the value of its optical rotation. No other natural occurrence of 2-C-methyl-D-erythritol has yet been reported. We now describe its characterization and its isolation from leaves of *Liriodendron tulipifera* L.

RESULTS AND DISCUSSION

In addition to the well-known series of inositols [4], the yellow autumn leaves of the tulip tree contain the ubiquitous carbohydrates sucrose, glucose and fructose; furthermore, we detected in our study an unusual, apparently small carbohydrate in these leaves, which, after isolation by PC on a small scale, yielded no-reducing properties and appeared to be an alditol. Subsequently, this compound was isolated from 500 g of leaves and crystallized to allow its identification. The ^{13}C and ^1H NMR spectra indicated that it was a C-methyltetritol; further comparison of the ^{13}C NMR spectrum and its physical properties with those published by Anthonsen *et al.* [1] showed that our compound was 2-C-methyl-D-erythritol. The ^{13}C NMR spectrum and the optical rotation are different from those of 2-C-L-threitol [3]. The ^1H NMR spectrum, which could not be resolved at 100 MHz by Anthonsen *et al.* [1], was fully analysed at 500 MHz.

The yield of crystalline 2-C-methyl-D-erythritol from yellow autumn leaves was 0.14% by leaf fresh weight; the young green leaves contain only traces of this compound, which apparently in autumn is shed with the leaves. Nothing is yet known about the biosynthesis of this branched-chain alditol. Anthonsen *et al.* [1] suggested that a C-methyltetrose or a C-methyltetrulose may be its precursor; but such sugars have not been reported to occur naturally. D-Apiose, a C-hydroxymethyltetrose, is

of widespread occurrence, but its deoxygenation and reduction would give 2-C-methyl-L-erythritol rather than 2-C-methyl-D-erythritol.

EXPERIMENTAL

Yellow-green autumn leaves of *L. tulipifera* (500 g) were extracted in an autoclave for 1 hr with hot H_2O (3l). The extract was concd under vacuum to a syrup which was then dissolved in 10% acetic acid (350 ml). Phenylhydrazine (50 ml) was added to ppt. the reducing sugars and the soln was boiled for 2 hr. To the mixture, after it cooled, acetone was added to remove excess phenylhydrazine. After standing in the refrigerator overnight, the mixture was filtered and the filtrate evapd to a syrup which was dissolved in H_2O and filtered through a column of activated carbon and celite. The now clear soln was deionized with Amberlite MB 3, concentrated to 40 ml and chromatographed on a column (750 ml) of carbon-celite (1:1). The fractions were monitored by descending PC on Whatman No. 1 with *n*-butanol-pyridine-HOAc- H_2O (60:40:3:30 by vol.). The last fractions emerging after those containing inositols were evaporated and the residue crystallized from aq. Me_2CO . Large crystals (700 mg) of 2-C-methyl-D-erythritol were obtained: mp 82° (lit. $82-83^\circ$ [1]). $[\alpha]_D^{20}$ 23.7° (H_2O ; c 1.37), 14.6° (MeOH; c 1.37) (lit. 21.4° (H_2O ; c 7.0) [1], 15.7° (MeOH; c 1.5) [2]). ^1H NMR (D_2O): δ 1.04 (3H, s, Me), 3.38 (d, $J_{1,2} = -11.7$ Hz, H-1), 3.495 (d, H-1'), 3.505 (dd, $J_{4,4'} = -11.5$, $J_{3,4} = 8.4$ Hz, H-4), 3.57 (dd, $J_{3,4'} = 2.6$ Hz, H-3), 3.745 (dd, H-4') (Bruker 500 in D_2O , reference dioxan at δ 3.67). R_f on ion-exchange TLC, Ca-form [5] 0.71, compared with 0.78 for erythritol.

REFERENCES

1. Anthonsen, T., Hagen, S., Kazi, M. A., Shah, S. W. and Tagar, S. (1976) *Acta Chem. Scand.* **B** 30, 91.
2. Anthonsen, T., Hagen, S. and Lwande, W. (1980) *Acta Chem. Scand.* **B** 34, 41.
3. Witczak, Z. J., Whistler, R. L. and Daniel, J. R. (1984) *Carbohydr. Res.* **133**, 235.
4. Angyal, S. J. and Bender, V. (1961) *J. Chem. Soc.* 4718.
5. Angyal, S. J. and Mills, J. A. (1985) *Aust. J. Chem.* **38**, 1279.