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Carbohydrate Research 339 (2004) 2731–2732
Carbohydrate RESEARCH

Note

1,5-Anhydroxylitol from leaves of *Olea europaea*

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Received 24 February 2004; received in revised form 7 April 2004; accepted 16 April 2004
Available online 12 October 2004

Dedicated in the memory of Professor Serena Catalano

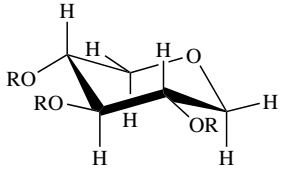
Abstract—1,5-Anhydroxylitol, a compound never found previously in the vegetal kingdom was obtained from *Olea europaea* leaves in ~0.5–1% yield.

Keywords: *Olea europaea* L.; 1,5-Anhydroxylitol; ^{1}H NMR; ^{13}C NMR; EIMS

Within an investigation about phylogeny and biodiversity of *Olea europaea*, the chemical investigation of the polar fractions of two cultivars (Frantoio and Cipressino) is in progress in our laboratory to identify in leaves extracts any compound of possible taxonomic value. This note reports the isolation and characterization from leaves of *O. europaea* of an anhydroalditol never previously found in the vegetable kingdom, 1,5-anhydroxylitol.

Dried leaves of *O. europaea* were successively extracted with hexane, chloroform and chloroform–methanol. Final extraction with methanol afforded a white sweet material (1.1% yield from cultivar Frantoio and 0.48% from Cipressino), which crystallized in ethanol. The ^{13}C NMR spectrum showed three signals at 63.9, 69.8 and 71.4 ppm that were sorted by DEPT experiments in one CH_2 and two CH, respectively. This situation was indicative of a cyclitol-like structure having a symmetry axis, and the $[\alpha]_D$ value of 0° confirmed a *meso* form.

Acetylation allowed to measure a first order ^{1}H NMR spectrum that showed a doublet at 5.72 ppm (1H, *J* 9 Hz), a multiplet at 5.42 (2H), a double doublet at 4.31 ppm (2H, *J* 12.5 Hz, *J* 2.6 Hz) and a double doublet at 4.03 ppm (2H, *J* 12.5 Hz, *J* 5.0 Hz). These data were in agreement with structure **1**, as confirmed also by the EI-mass spectrum of the acetylative derivative **1a**, where a molecular peak at *m*/*z* 260 was present.



1 R = H
1a R = Ac

The structure of 1,5-anhydroxylitol (**1**) was further confirmed by comparison of the physico-chemical data for **1** and **1a** with the literature.[1–3]

1. Experimental

1.1. Material and methods

Leaves of *O. europaea*, cultivar Frantoio and cultivar Cipressino, were collected in the experimental field of Dipartimento di Coltivazione e Difesa delle Specie Legnose, Facoltà di Agraria, University of Pisa.

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doi:10.1016/j.carres.2004.09.001

^{1}H and ^{13}C NMR data were obtained with a Bruker AC 200 instrument working at 200.13 MHz for ^{1}H and at 50.33 MHz for ^{13}C.

1.2. 1,5-Anhydroxylitol

The dried leaves (560 and 340 g for Frantoio and Cipressino, respectively) were successively extracted in a Soxhlet apparatus with hexane (1.5 L), $CHCl_3$ (1.5 L) and 9:1 $CHCl_3$–MeOH (1.5 L).

The last extract was suspended in MeOH; the soluble portion, after concentration yielded a white sweet water-soluble powder (6.16 g, yield 1.1% for cv Frantoio and 1.62 g, yield 0.48% for cv Cipressino), which was dissolved in hot EtOH and allowed to cool slowly to obtain a crystalline material **1** that was then filtered; mp 110–112 °C, lit.[1] 116–117 °C, lit.[2] 113.5–115.5 °C, lit.[3] 90–91 °C; ^{13}C NMR (Me_2SO): δ 71.43 (C-3), 69.78 (C-2, C-4), 63.95 (C-1, C-5); ^{13}C NMR (D_2O): δ 59.86 (C-3), 59.61 (C-2, C-4), 56.82 (C-1, C-5), identical with lit.[3]

Acetylation of **1** (0.300 g of **1** were suspended in a mixture of 2:1 pyridine–Ac_2O (50 mL) at room temperature for 24 h under stirring; the soln was evaporated to dryness and the residue was washed with toluene three times and crystallized from EtOH) yielded **1a**, mp 120 °C, lit.[1]122–123 °C; ^{1}H NMR (C_6D_6) δ: 5.72 (1H, d, J 9.0 Hz, H-3), 5.42 (2H, m, H-2, H-4), 4.31 (2H, dd, $J_{1e,1a}$ and $J_{5e,5a}$ = 12.5 Hz, $J_{1e,2}$ and $J_{5e,4}$ 2.6 Hz, H-1e, H-5e), 4.03 (2H, dd, $J_{1a,1e}$ and $J_{5a,5e}$ 12.5 Hz, $J_{1a,2}$ and $J_{5a,4}$ 5 Hz, H-1a, H-5a), 1.79 (3H, OCH_3), 1.72 (3H, OCH_3), 1.69 (3H, OCH_3); EIMS: *m/z* 115, 145, 187, 217, 260.

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