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6-O-OLEUROPEOYLSUCROSE FROM OLEA EUROPAEA[(+)]

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It was shown in an earlier paper (1) that oleuropeic acid (I), 4-(1-hydroxyisopropyl)-1-cycloexene-1-carboxylic acid, occours in the roots bark of Olea Europaea, mainly as a sucrose ester (II).

We wish now to demonstrate the position of the ester linkage.

Selective acidic hydrolysis (1N H_2SO_4, 24 h at room temperature) or enzymic hydrolysis (invertase) yielded fructose and a compound with chromatographic properties differing from those of both (I) and (II). This compound, which reacted positively either with benzidine reagent or antimony trichloride on the paper chromatogram, is evidently a glucose ester of (I); hence, in the molecule of oleuropeoyl sucrose, oleuropeic acid is bound to the glucose unity.

When submitted to periodic oxidation, under conditions that exclude the possibility of hydrolysis of the ester linkage (using M/10 $NaIO_4$ at room temperature, reaction was complete in 90 minutes), oleuropeoyl sucrose consumed three moles of reagent. The same reaction was also carried out on sucrose, in order to check its behaviour, under the adopted conditions (see table I)

These data, in addition to reported results of hydrolysis, show that oleuropeic acid is linked to the -OH

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at C_6 of glucose unity(+); compound (II) is therefore 6-O-oleuropeoylsucrose.

TABLE I

Time in Minutes	Moles of HIO_4/Moles of Substrate	
	Sucrose	oleuropeoylsucrose
30	2.93	2.66
90	3.02	3.03
270	3.13	3.10

Supporting evidence of this structure was obtained by comparison of NMR spectra of oleuropeoyl sucrose and of sucrose. In spectrum of (II) (measured in hexadeuterodimethyl-solfoxide at 100 Mc(++), external reference hesamethyldisiloxane) a complex multiplet, centered at δ = 4.71, not imputable to oleuropeoyl protons, appears at a field, where no signals are shown by sucrose; at the same time a strong peak of sucrose, at δ = 3.97, desappears. Integration of the shifted signals at δ= 4.71 corresponds with a good approximation to two protons, according to the existence of the ester linkage on a primary hydroxy group.

(+) If the O-acyl-group had been attached at C_2, C_3 or C_4 of glucose, two, one or two moles of reagent would have been consumed, respectively.

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REFERENCES

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