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## 2-methyl-but-3-en-2-yl-I-O-ß-D-glucopyranoside from Bergenia crassifolia and strachey

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**Chimica.** — *2-methyl-but-3-en-2-yl-1-O-β-D-glucopyranoside from* Bergenia crassifolia *and* strachey. Nota di PAOLA ESPOSITO (*) e MARCELLO NICOLETTI (**), presentata (***) dal Corrisp. G. B. MARINI-BETTÒLO.

RIASSUNTO. — Dalle foglie di *Bergenia crassifolia* e *strachey* (saxifragaceae) è stato isolato il 2-metil-but-3-en-2-il-1-O-β-D-glucopiranoside. Viene inoltre discusso il possibile ruolo biologico e biogenetico del composto isolato.

2-methyl-but-3-en-2-ol *1* has been the subject of great attention since it was identified as the essential sexual attractant of *Ips tipographus* [1]. In fact, *1*, in a mixture with other terpenic substances, was used in 1979 in Norway and Sweden in a large program to control damage caused by beetles to Norwegian spruce trees [2]. Interestingly, it is assumed that these pheromones derive from metabolism by the beetles of terpene components present in the tree host. In consideration of its possible biological role, we report the isolation in a good yield of β-D-glucoside of *1*, *2*, from the leaves of *Bergenia crassifolia* and *strachey* (Saxifragaceae). *2* has been already isolated from *Ferula loscosii* WK., an endemic Spanish Umbellifera [3].

The structure of *2* was determined by analysis of the $^1H$ NMR spectra of *2*, of the tetraacetyl derivative *3*, of the dihydro derivative *4* and of the tetraacetyl derivative of *4*, *5*. The coupling constant of H-1′ anomeric proton ($J = 7.5$ Hz) was diagnostic of a β-glucosidic linkage, confirmed by reaction with β-glucosidase affording glucose (chromatographically identified) and the compound *1*. Acid hydrolysis of *2* gave glucose, *1* and a small amount of 3-methyl-but-2-en-1-ol *6*. *1* and *6* were identified by GLC comparison with authentic samples. Finally, the reaction of *1* with 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside in the presence of $Ag_2CO_3$ afforded *3*.

The most interesting feature of this finding is that this pheromone is present in plants in the form of glucoside. Its structural relationship to the isomers 3-methyl-but-2-en-1-ol and 3-methyl-but-3-en-1-ol, which as phosphates (dimethylallyl- and isopentenylphosphate, respectively) appear in the biosynthesis of terpenes and terpenoids, may suggest a particular role of this compound also in plant and animal metabolism.

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## Experimental

Isolation — 3.7 kg of fresh leaves were extracted with MeOH (10 l) for 2 days at room temperature. A paper chromatogram showed *2* as a blue spot (Rf 0.65) (hydrochloric vanillin as reagent, *n*-BuOH/AcOH/$H_2O$ 63 : 10 : 27 v/v/v as eluent). The extract was concentrated and purified by chromatography on silica gel (BuOH sat. $H_2O$). *2* (0.5 g) was obtained by crystallization from $CH_3COOEt$ (needles). M.p. 146-7 °C. $^1H$ NMR ($D_2O$, $\delta$): 1.11 and 1.22 (6 H, s, $(CH_3)_2C$), 4.51 (1 H, d, J = 7.5 Hz, H–1′), 5.22 (1 H, dd, J = 10.3 and 1.7 Hz, $H_A$–4), 5.29 (1 H, dd, J = 17.6 and 1.7 Hz, $H_B$–4), 6.02 (1 H, dd, J = 17.6 and 10.3 Hz, $H_X$–3).

## References

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