

NOVEL DIMERS IN SCENT GLANDS OF THE BARK BUG PHLOEA SUBQUADRATA

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ABSTRACT. Bark bugs belonging to the family Phloeidae are known for their camouflage devices on tree trunks. The defensive secretion stored in dorsal abdominal glands of nymphs has a pungent odor and is mainly constituted by (*E*)-2-hexenal, (*E*)-2-octenal and (*E*)-4-oxo-2-hexenal. Metathoracic glands of adults (male and female) store particularly (*E*)-2-hexen-1-ol and (*E*)-2-hexenyl acetate, which are compounds less irritating than the corresponding aldehydes. However, additional compounds were detected in the scent glands of this bug species, many of which are still unknown. Thus, the aim of this study was to elucidate the chemical structure of the dimers (*m/z* 224) found in scent glands of *Phloea subquadrata*. Gland content from adults was removed with a micro-syringe and submitted to GC-MS and NMR analyses, revealing the presence of (*E*)-4-oxo-2-hexenal (*m/z* 112) and four unknown dimers (*m/z* 224). (*E*)-4-oxo-2-hexenal was obtained from furfural and in the purification process was transferred to a silica column and the fractions were monitored by GC-MS, revealing the monomer and four compounds of *m/z* 224. Based on the NMR analysis (¹H, ¹³C, DEPT 135, DEPT 90, HSQC, HMBC, NOESY and COSY) of the dimer mixture of about 3:1 ratio. A synthetic mixture of the products co-eluted with the natural products. The proposed structures for these two dimers have not shown any similarity to any previously reported bug compounds.