

Chemistry of the Calceolaria Genus. Structural and Biological Aspects

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Abstract: Autochthonous species of the Calceolaria (Scrophulariaceae) genus are studied. From their apolar extracts 55 new diterpenes of six skeleton types, naphthoquinones and flavonoids have been isolated. Among the different diterpenes malonic substitutions and bis-diterpenes in which both units are joined by a malonic acid unit stand out. Pimaranes present C-9 epimerisation and, consequently, H-9 has the same orientation as Me-20. From *C.sessilis* naphthoquinones with anti-chagasic activity have been isolated; and the biotransformation of 2 α ,19-dihydroxy-9-epi-ent-pimara-7,15-diene with *Giberella fujikuroi* produced 7 new diterpenes.

The Calceolaria genus is one of the most abundant of the Scrophulariaceae family. According to Engler [1] there are more than 5000 species distributed throughout New Zealand and especially, Central and South America. Some 86 species grow in Chile [2] and several of them are badly defined. They are known by the common names “capachito”, “zapatito” and “topa-topa”, and they are used in popular medicine as stomach tonics, bactericidal agents and sweeteners.

In a systematic study of the secondary metabolites of the genus 19 autochthonous species have been studied, with particular attention being paid to the geographical-botanical surroundings of Valparaíso (Region V).

From the apolar extracts we have isolated a series of 55 new diterpenes belonging to six skeletal types, naphthoquinones y flavonoids [3-14].

Among the different diterpenes isolated, the presence of malonic esters and bis-diterpenes- 5 with a pimarane skeleton - in which both units are joined by a malonic acid molecule is worth mention.

The biogenetic mechanism of cyclization of the pimaranes takes place via adoption of “chair-boat” conformation, instead of a “chair-chair” one, usually found in Nature [3]. This mechanism leads to an epimerization of C-9 and, consequently, H-9 is found in the same orientation as the Me-20 group. From *C. sessilis* we obtained naphthoquinones that displayed promising trypanocidal properties [10]. Finally, the biotransformation of 2 α ,19-dihydroxy-9-epi-ent-pimara-7,15-diene with *Gibberella fujikuroi* produced 7 new diterpenes [15] among which oxidation of the diene at C-7 is prevalent.

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References and Notes

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