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Recent Advances in the Chemistry of Chilean Lichens (**)

Introduction

Lichens, a symbiotic association between fungi and algae, have their own characteristics, which make them different from their precursors in their morphologic, physiologic, and ecologic aspects.

Lichens are highly sensitive to permanent humidity conditions, and they are not able to accumulate water; they constantly depend on their surroundings for its supply. They are not found near industrial zones due to their considerable sensitivity to toxic gases. This property is used as a biological indicator for environmental pollution. They react to the presence of even minute quantities of pollutants, with structural modifications which can cause their disappearance far earlier than the appearance of minimal contamination symptoms in other organisms of the surroundings.

Their biological action is well known, and this knowledge goes back to the ancient Egyptians and Greeks. During the 15th century lichens became an important commercial item in Europe. Mixtures of Icelandic lichens, such as *Cetraria islandica*, *Lobaria pulmonaria*, and *Cladonia* species were used for the treatment of catarrhal haemoptysis and lung tuberculosis.

Later on, the study of these lichens demonstrated the soundness of their use in those treatments, due to the discovery of new compounds in them — especially depsides, depsidones and dibenzofurans — which possess antibiotic activity.

The chemical study of secondary metabolites isolated from lichens was started at the beginning of this century [1, 2]; but the researches of Asahina and Shibata [3], Culberson [4, 5], Huneck [6, 7], and Elix *et al.* [8] going on since

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(**) Presented at the International Congress on « Medicinal Plants » (Sanrepolcro (AR), 17-19 October - Roma, October 20th 1987), organized by the Accademia Nazionale delle Scienze detta dei XL.

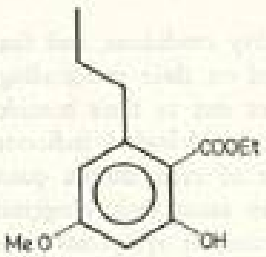
1954, have revised and systematized the knowledge of their structures, properties and distribution.

As happened in all fields of the chemistry of natural products, progress has been achieved due to the enormous improvement of the methods for detection, isolation, and structure elucidation.

Secondary metabolites of Chilean Lichens

The chemical study of secondary metabolites isolated from continental Chilean lichen species which our laboratory has been undertaking since 1983, has, so far, permitted the investigation of 23 species; 5 new [9-11] and 25 already known [12-14] compounds have been isolated from them.

In particular, details on the research on *Protousnea malacea* [9], *Cornicularia epiphorella* [10], and *P. magellanica* [11], from which the new substances have been isolated, are presented. For the establishment of their structures the use of nuclear magnetic resonance of ^{13}C has been relevant.



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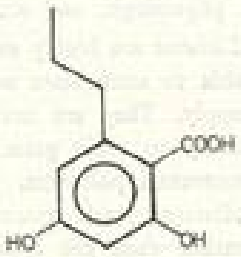

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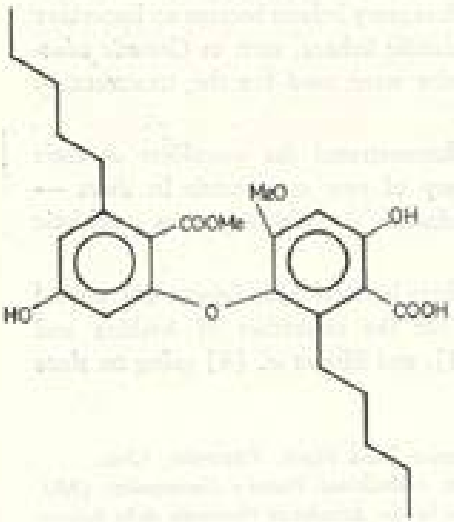

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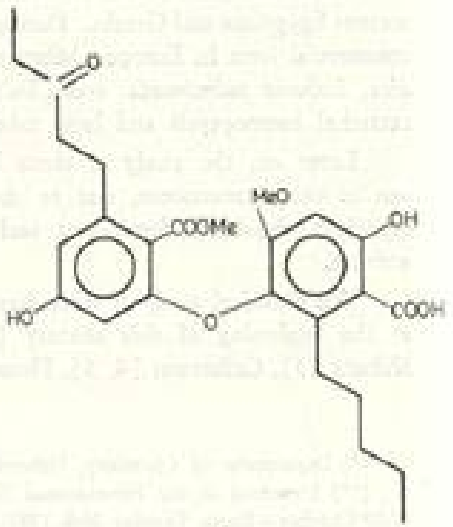

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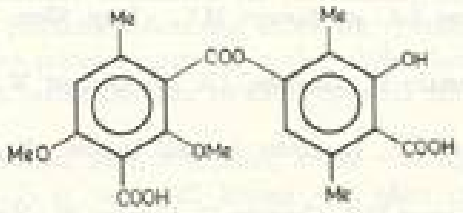
Two new mononuclear phenolic compounds have been isolated from *P. malacea* (Parmeliaceae): ethyl divaricatinate (**1**) and divaric acid (**2**).

The study of *Cornicularia epiphorella* (Usneaceae) led to the isolation of two new diaryl ether structures: epiphorellic acids 1 (**3**) and 2 (**4**). The isolation and structural study of this type of ethers has been known for the last 10 years only, due to the work of Foo [15, 16], and Elix [17-20].

Acids **3** and **4** are the first detected in American lichens. Their structures were established by chemical correlation and the use of ^{13}C-NMR.

Compound **3** has shown interesting results with respect to antibacterial and antifungal action [21, 22].

During this last year *Protousnea magellanica* has been studied (Parmeliaceae). This is a lichen whose habitat is the trunks of *Nothofagus*. From it 2'-0-methyl-squamatic acid (**5**) was isolated, a new depside derivative of β-orcinol. Its structure was basically established by spectrophotometric analysis of its methyl ether.



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