Flavonoids of Gnaphalieae: *Leontopodium alpinum* Cass

Following our previous work on flavonoids of Gnaphalieae (Asteraceae ex Compositae)[1,2] we have now investigated the flavonoids of *Leontopodium alpinum* Cass, the worldrenowned 'Edelweiss'.

Very little information is reported in the chemical literature about this plant: the leaves and flowers are described as containing a glycosidic substance, poisonous to the frog and mouse[3–5]. According to PETROVSKII[6], the congenerial yellow *Leontopodium ochroleucum* behaves as colagog agent.

From the methanolic extract of defatted samples of *Leontopodium alpinum*, collected at an altitude of about 1500 m in Piemonte, Val Chisone, in summer 1968, we have isolated, by column chromatography on Silicagel, a flavonoid-rich fraction, showing 3 Benedikt's reactive spots, respectively Rf 0.81/0.63 and 0.43 in BAW (*n*-butanol : acetic acid : water 4:1:5).

The separation of the flavonoids is easily accomplished by chromatography on polyammide powder[7] with increasing methanol-water mixtures and preparative paper chromatography.

We have identified the flavone Rf 0.81 in BAW, as luteolin (3′,4′,5,7 tetrahydroxyflavone) by physical constants and spectral properties, and confirmed via direct comparison with an authentic specimen[8].

The flavones Rf 0.63 and Rf 0.43 in BAW, which are glycosidic in nature (glucose identified by TLC after hydrolysis) compare, as regards their physical and chemical properties, with the respectively 4′- and 7-*O*-*β*-D glucosides of luteolin, previously characterized in *Antennaria dioica* Gaertn[2].

To our knowledge this is the first report of flavonoid analysis in *Leontopodium* species.

Noteworthy, from the taxonomical point of view, is the presence of the scarcely distributed luteolin 4′-*O*-*β*-D glucoside (at present time only referred in *Sparteum junceum*[9], *Pirus ussuriensis*[10] and *Acer cissifolium*[11]), particularly if compared with the presence of this substance in Gnaphalieae-belonging *Antennaria dioica*[2] and *Gnaphalium annum*[12].

Riassunto. Dalla stella alpina (*Leontopodium alpinum* Cass, Gnaphalieae-Asteraceae) vengono isolati la luteolina (3′,4′,5,7 tetraidrossiflavone) ed i suoi 4′- e 7-*O*-*β*-D glucosidi.

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Wagner-Meerwein Type Rearrangement of 2-Hydroxypinocamphone: Conversion of Pinane Skeleton into Oxapentalane System

In connection with the study on stereochemistry of 2-hydroxypinocamphone (I)[1,2], this hydroxy-ketone was treated with anhydrous oxalic acid. We have now found that the hydroxy-ketone I was converted into dihydro-*β*-campholenolactone (II) with an oxapentalane skeleton by a Wagner-Meerwein type rearrangement. This is an unique example of an alteration of a pinane skeleton by an acid-catalyzed reaction.

A mixture of I (1.2 mole; mp 34–35 °C, $[\alpha]_D^{25}$ – 23.26°) and anhydrous oxalic acid (4.6 mole) in acetone was refluxed for 6 h. The neutral reaction mixture obtained after usual treatment was subjected to a fractionation to isolate *γ*-lactone II [31% yield; mp 30–31 °C ([3] mp 32 °C); $[\alpha]_D^{25}$ – 12.70° (c 9.9, MeOH); $\nu_{C=O}$ 1774 cm^{-1} ([4] 1786 cm^{-1}); λ_{max}^{MeOH} 210 nm (ε 44.6); *m/e* 168 (M^+)], accompanied by a trace of *δ*-lactone III.

The identity of the lactone II with dihydro-*β*-campholenolactone was proven by comparing its spectra with those of an authentic sample[5], and further by the conversion into 1-(2-hydroxyethyl)-2,3,3-trimethyl-2-cyclopentanol [mp 147–148 °C ([3] mp 147 °C)]. In order to decide the stereochemistry, we first relied on the solvent effect of the NMR-spectrum: *a*-, *b*- and *c*-Methyl signals of II were observed to suffer shifts by + 0.43, + 0.39 and + 0.11 ppm by changing a solvent from deuteriochloroform to benzene[7] and by + 0.17, + 0.27 and – 0.08 ppm to pyridine[8], respectively. The lactone ring of II was thus found to take *cis*-form and the stereochemistry is therefore assigned as either IIa or its optical antipode (IIb). According to the lactone sector

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