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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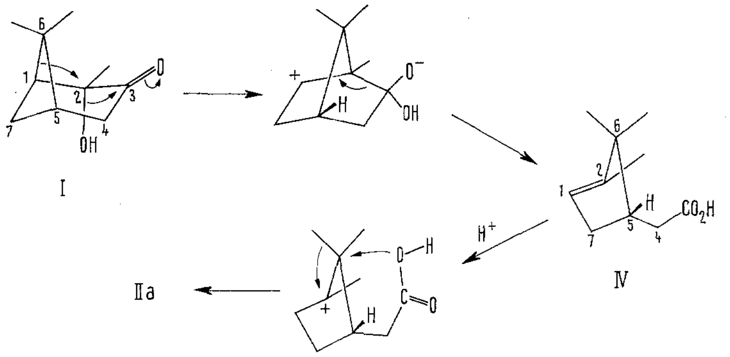
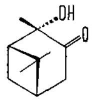
rule[9], IIa should exhibit a negative and IIb a positive Cotton effect. The ORD and CD curves were then found to exhibit the negative Cotton effect: $[\phi]_{225}^{\text{shoulder}}$ −1550° (in MeOH); $[\theta]_{210}^{max}$ −328° (in MeOH). The stereochemistry of (−)-dihydro-β-campholenolactone (II) was consequently clarified to be IIa.

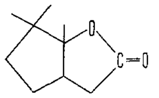
In order to clarify the mechanism of formation of lactone II from the hydroxy-ketone I, the acetone solution of I was treated with anhydrous oxalic acid during a shorter reaction time in the same manner as above. The formation of (−)-α-campholenic acid (IV) expected as an intermediate was proven by isolation from the reaction mixture in 6% yield. On the other hand, treatment of (+)-α-campholenic acid (IV) with anhydrous oxalic acid under the same conditions was found to yield (+)-γ-lactone II (41%) and (−)-1,2-campholide (III) (22%). α-Campholenic acid (IV) was thus evidenced as an intermediate product to produce γ-lactone II from hydroxy-ketone I.

The formation of dihydro-β-campholenolactone (II) is best explained as involving the Wagner-Meerwein type rearrangement of I to the intermediate IV, which then undergoes protonation at an ethylenic bond, 1,2-shift of a methyl group, and lactonization to yield II, as shown in the Scheme. On the other hand, the formation of 1,2-campholide (III) from α-campholenic acid is interpreted as undergoing lactonization between the carboxyl group and the C-2 carbon of the carbonium ion. These reactions support the supposition that the C-2 methyl group of 2-hydroxypinocamphone (I) is *cis* with respect to the gem-dimethyl bridge, as discussed recently in our paper[2].

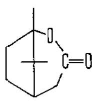




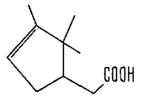
I



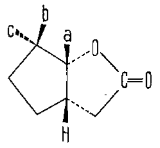
II



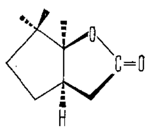
III



IV



IIa



IIb

Zusammenfassung. Die Reaktion von (−)-2-Hydroxypinocamphon (I) mit wasserfreier Oxalsäure in Aceton liefert (−)-Dihydro-β-campholenolakton (IIa). Die Stereochemie liess sich durch NMR-, ORD- und CD-Spektren bestimmen. Es wird ein Reaktionsmechanismus diskutiert.

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Identification of Odorous Compounds from Male Lepidoptera

Males of many species of Lepidoptera emit odorous compounds from specialized scales, 'hair pencils' or brush-organs. Males of the nocturnal moth, *Phlogophora meticulosa* (L.) release scent to induce the female to copulate[1] and about $^1/_3$ of the 300 British Noctuidae have similar brushes to those described from *P. meticulosa*[2], consisting of paired abdominal glands, brushes and storage pockets. The brushes store and disperse scent synthesized in glands remote from them so that only the final secretion product occurs on the brushes.

Method. Each brush was cut across its base while still in the pocket, carefully removed so that very little scent was lost, and extracted in carbon tetrachloride. Solutions were analyzed in the first instance by gas chromatography and the components identified using combined gas-liquid chromatography (GLC)-mass spectrometric methods[3]. All components so identified were commercially available or easily synthesized for control purposes. We thank Dr. W. H. McFadden (I.F.F.; USA) for comparing one of our spectra with his reference collection and for supplying a sample of pinocarvol for oxidation to pinocarvone.

Results. The identities and relative proportions of the compounds isolated from the brushes of 8 species of Noctuidae are given in the Table.

We had previously shown that benzaldehyde is the major component of the scent in 2 *Leucania* species[4], but the minor component, iso-butyric acid, was then undetected. Males of *Bapta temerata* (Schiff.) in the family Geometridae secrete *n*-butyric acid apparently for the same function. The first two components from *P. meticulosa* which we had previously thought to be a single compound near benzaldehyde, are now found to be

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