Constituents of *Helenium plantagineum*

By MARIO SILVA

From flowers of *Helenium plantagineum* four compounds were isolated—a polymethylenic alcohol, β-sitosterol, linifolin A, and deacetoxylinifolin A.

In recent years there has been considerable interest in the study of the constituents of the *Helenium* genus (1–5).

During a current project dealing with Chilean flora (6) the authors had occasion to re-examine *Helenium plantagineum* (D.C.) Macbride in order to study the compounds isolated by Taito (7).

The petroleum ether soluble fraction yielded four compounds characterized as: a high molecular weight aliphatic alcohol, which was not further studied; β-sitosterol; linifolin A (8); and deacetoxylinifolin A. Deacetoxylinifolin A was also isolated through crystallizations from the benzene soluble fraction.

EXPERIMENTAL[1]

Petroleum Ether Extract—Flowers of *Helenium plantagineum*, collected in January 1962 near Florida (Concepción), were dried at 80–90°. A 2064-Gm. quantity of dried powder was extracted to exhaustion in a Soxhlet extractor with petroleum ether (b.p. 65–75°). This solution was concentrated to yield 461 Gm. of a dark product. This product was chromatographed many times on neutral alumina to give four compounds. The first compound is probably a polymethylenic alcohol, m.p. 78°, $[\alpha]_D$ 0° (chloroform, c 1), molecular weight 432 (Rast), which was not further studied.

β-Sitosterol—After several crystallizations of the second compound from ethanol, β-sitosterol was obtained, m.p. 137–138°, $[\alpha]_D$ −33.5° (chloroform, c 0.39), $\nu_{max.}^{KCl}$ 3380 cm.$^{-1}$.

The mixed melting point of this compound with authentic β-sitosterol showed no depression.

β-Sitosterol Acetate—The pure compound was obtained as needles after crystallizations from ethanol, m.p. 128–129°, $[\alpha]_D$ −49° (chloroform, c 0.43), $\nu_{max.}^{Nujol}$ 1736, 1250 cm.$^{-1}$.

Linifolin A—From the third product, through crystallizations from ethanol, 167 mg. of linifolin A was obtained, m.p. 202–203°, $[\alpha]_D$ +28.1° (chloroform, c 0.39), $\lambda_{max.}^{EtOH}$ 217 mμ, ϵ 13000, $\nu_{max.}^{Nujol}$ 1745, 1706, 1658, 1590, and 1235 cm.$^{-1}$.

Anal.—Calcd. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.35; H, 6.36.

This compound did not show depression with an authentic sample of linifolin A on mixed melting point determination.

Deacetoxylinifolin A—The fourth compound, after recrystallizations from ethanol, gave 250 mg. of deacetoxylinifolin A, m.p. 251°, $[\alpha]_D$ +58.4° (pyridine c 0.38), $\lambda_{max.}^{EtOH}$ 217 mμ, ϵ 15150, $\nu_{max.}^{Nujol}$ 3717, 1745, 1698, and 1582 cm.$^{-1}$.

Anal.—Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.48; H, 7.00.

Deacetoxylinifolin A Acetate—Deacetoxylinifolin A on acetylation with pyridine–acetic anhydride at room temperature gave, after crystallization from methanol–chloroform, the acetate, m.p. 194°, $[\alpha]_D$ +28.8° (chloroform, c 0.52), $\lambda_{max.}^{EtOH}$ 217 mμ, ϵ 14400, $\nu_{max.}^{Nujol}$ 1745, 1706, 1658, 1590, and 1236 cm.$^{-1}$.

This acetate did not show depression with an authentic sample of linifolin A on mixed melting point determination.

Benzene Extract—The defatted plant material was dried and the benzene soluble constituents were extracted. This solution was concentrated to yield 80 Gm. of a dark product. This product, after several recrystallizations from ethanol, yielded 2.5 Gm. of deacetoxylinofolin A, m.p. 253–254°, $[\alpha]_D$ +59° (pyridine, c 0.7).

The mixed melting point of this compound with deacetoxylinifolin A, previously isolated, showed no depression.

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[1] Melting points (uncorrected) were performed on a Kofler block. Rotations were measured at 20°. The microanalyses were performed at Dr. Alfred Bernhardt's Institute, Ruhr, Germany. Ultraviolet spectra were recorded in solution in absolute ethanol on a SP 700 spectrophotometer. Infrared spectra were recorded on a Perkin Elmer 137 spectrophotometer.

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