SACCHARINIC ACID LACTONE<sup>(1)</sup> FROM <u>ASTRAGALUS LUSITANICUS</u> LAM.<sup>(2)</sup> (-)-2-C-METHYL-D-ERYTHRONO-1,4-LACTONE

J. de Pascual Teresa<sup>\*</sup>, J.C. Hernández Aubanell, A. San Feliciano and J.Mª Miguel del Corral Departamento de Química Orgánica. Facultad de Ciencias. Salamanca. Spain.

Abstract: (-)-2-C-methyl-D-erythrono-1,4-lactone has been isolated from <u>A. lusitanicus</u>, its structure being established by spectroscopic methods and synthesis. This is the first report of a natural saccharinic acid lactone.

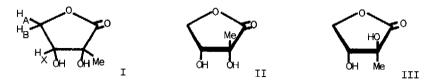
Iberian milk-vetch (<u>Astragalus lusitanicus</u> Lam. fam. Leguminosae) is a "loco-weed" that grows in Portugal and the West of Spain. It shows a high degree of toxicity for cattle and no report on its chemical composition appears to have been made.

The ethanolic extract form the aerial part of the plant gave negative response to the Gries-Ilosvay test for nitroderivatives. It was concentrated and dispersed into water, after which it was extracted with ether and <u>n</u>-BuOH and finally the water was removed from the aqueous solution at reduced pressure.

By chromatography of the brown syrup obtained on silica gel and elution with  $CHCl_3/EtOH$ (9:1), we have isolated a small amount of a new natural lactone whose MS (M<sup>+</sup>, m/e = 132) and elemental analysis correspond to the molecular formula  $C_5H_8O_4$ . Its IR spectrum (film) has absorption maxima at  $\mathcal{M}(cm^{-1})$ : 3500, 1770, 1200, 1100 and 1030 ( $\gamma$ -lactone and -OH groups). The <sup>1</sup>H NMR spectrum ( $C_5D_5N$ ) shows signals at  $\mathcal{S}ppm$ : 1.39 (3H, s) of Me- $\dot{C}_7$ -OH and 4.1-4.6 (2H, complex multiplet).

Acetylation (Ac<sub>2</sub>O/NaOAc reflux), gives a diacetate  $\left[m.p. 86-7^{\circ}C, \left[\alpha'\right]_{D} = -9^{\circ} (\underline{c}, 0.9 \text{ CHCl}_{3})\right]$ , whose IR spectrum shows no bands for -OH groups and whose <sup>1</sup>H NMR spectrum has signals at  $\delta$ ppm: 1.67 (3H, s; <u>Me</u>- $\zeta$ -OAc), 2.07 and 2.13 (two Me-COO- singlets), 4.5 (2H, octet, AB part of an ABX system) and 5.35 (1H, q; X part.  $J_{AB} = 10.5 \text{ Hz}$ ,  $J_{AX} = 6.2 \text{ Hz}$  and  $J_{BX} = 4 \text{ Hz}$ ).

All preceding data, as well as the fragmentation pattern in the MS of both substances:  $\gamma$ -lactone, m/e (%): 132 (2.5), 117 (5), 104 (5), 85 (95), 83 (100), 74 (33), 70 (35) and 55 (22). Diacetate: 216 (7), 172 (8.5), 149 (7.5), 146 (8), 130 (48), 129 (52), 112 (7.5), 103 (13.5), 74 (20), 70 (18), 55 (13) and 43 (100), <sup>(3)</sup> support structure I for the lactone.



On treating D-xylose with  $Ca(OH)_2$ , Ishizu, Lindberg and Theander<sup>(4)</sup> obtained, among other compounds, lactones II and III. They reported that the <u>erythro</u>-lactone II gives a cyclic ketal with acetone/H<sub>2</sub>SO<sub>4</sub>/CuSO<sub>4</sub>, but the <u>threo</u>-lactone III does not. Furthermore, only II gives a positive reaction with periodate-benzidine reagent. Thus, the relative configuration of the natural lactone is <u>erythro</u> because it gave a positive test with periodate-benzidine and also produced an isopropylidene derivative [m.p. 40-1°C,  $[\alpha]_D = -99°$  ( $\underline{c}$ , 0.85, CHCl<sub>3</sub>] whose IR and <sup>1</sup>H NMR spectra were identical to those of a synthetic sample [oil,  $[\alpha]_D = -22°$  ( $\underline{c}$ , 2.2, CHCl<sub>3</sub>] prepared by us trough the same reaction as of Ishizu <u>et al.</u><sup>(4)</sup> followed by ketalization, solvent fractionation and chromatography.

The  $[\alpha]_{D}$  reported for II and its cyclic ketal are -18° (<u>c</u>, 0.2 water) and -40° (sol ?) but, according to the fragment-recombination and other proposed mechanisms, <sup>(1)</sup> partial racemization is produced during the alkaline reaction. Thus we may conclude that the natural lactone,  $[\alpha]_{D} = -58.6^{\circ}$ (<u>c</u>, 0.68, water), has the configuration of II, (2<u>R</u>,3<u>R</u>) 2,3-dihydroxy-2-methyl- $\gamma$ -butyrolactone, or 2-C-methyl-D-erythrono-1,4-lactone.

The 3-monobenzoylated derivative  $[m.p. 144-5^{\circ}C, [\alpha]_{D} = -80^{\circ} (\underline{c}, 0.43, CHCl_{3})]$  has also been prepared. <sup>1</sup>H NMR spectrum  $\delta$ ppm: 1.6 (3H, s), 4.5 (2H, m), 5.4 (1H, q) and 7.3-8.2 (5H, m).

From more polar fractions, eluted from the initial chromatographic column with  $CHCl_3/EtOH$  (1:1), we have isolated (+) pinitol, m.p. 186-7°C,  $[\alpha]_{n} = +65^{\circ}$  (0.78, water).

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