PONDRANEOSIDE, A NEW IRIDOID GLUCOSIDE FROM *PONDRANEA RICASOLIANA*

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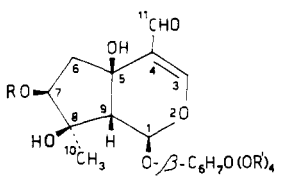
ABSTRACT.—*Pondranea ricasoliana* (Tauf) Sprague (Bignoniaceae) contains a new iridoid glucoside, pondraneoside (**1**). Its structure has been demonstrated by ^{13}C-nmr analysis and by transformation into lamiidol (**4**).

As it is well known that many plants of the Bignoniaceous family contain iridoid glucosides, we examined the ethanolic extracts of a creeper belonging to a genus of this family not investigated until now, the *Pondranea ricasoliana* (Tauf) Sprague, a plant characteristic of the subtropical zone. We isolated two new iridoid glucosides (1) both with very high Rf value and pale pink lilac reaction with vanillin reagent. Here we report on the structure and configuration of the most polar compound (**1**) which we named pondraneoside.

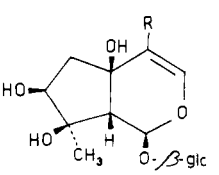
RESULTS AND DISCUSSION

Compound **1** is an amorphous powder with $[\alpha]_D = -69.2°$ and the molecular formula $C_{25}H_{30}O_{12}$. Its acid hydrolysis afforded glucose (one mole) and insoluble tars due to decomposition of the aglycone. The ir spectrum of **1** showed bands at 2730 (s), 1720 (s), 1685, 1665, 1650, 1635 cm^{-1} and the uv spectrum showed absorptions at 222 (log $\epsilon = 4.3$), 243 (log $\epsilon = 4.3$) and 277 (log $\epsilon = 4.3$) nm. These data suggested the presence of both unsaturated ester and aldehydic functions in the molecule of **1**. The alkaline hydrolysis of **1** allowed the isolation of the *trans* cinnamic acid, identified by its ^{1}H-nmr and uv spectra. The ^{1}H-nmr of **1** (see experimental) supports an iridoidic structure and shows, as major features: a) the presence of the *trans* cinnamoyl residue (two one-proton doublets at 6.44 and 7.64 ppm with $J = 16$ Hz and an aromatic protons multiplet between 7.7–7.2 ppm); b) an unsaturated aldehydic function (one proton singlet at 9.10 ppm) which must be linked to C–4 as the H–3 proton is very deshielded, appearing among the aromatic protons 7.7–7.2 ppm; c) a methyl group at C–8 geminal with a hydroxyl function (three protons singlet at 1.09 ppm). The two one-proton singlets present in this spectrum at 5.85 and 2.82 ppm are attributable to H–1 and H–9, which do not show a measurable coupling constant.



1 R=trans-cinnamoyl, R'=H

2 R=trans-cinnamoyl, R'=Ac



3 R=COOCH$_3$

4 R=CH$_2$OH

The lack of any measurable coupling constant in the H–9 signal allows the exclusion of the presence of the H–5. The two-proton signal pattern centered at 4.75 ppm, which appears shifting the HDO signal by heating the sample at 70°, is attributable to two superimposed signals: those of H–1' and of the proton geminal with the cinnamic ester function. Finally, the broad two-proton signal centered at 2.33 ppm is attributable to a methylene group in the cyclopentane ring.

Acetylation of **1** in mild conditions gave the tetraacetate **2**, still showing OH bands in the ir spectrum. Its ^{1}H-nmr spectrum (see experimental) showed the

TABLE 1. ^{13}Cnmr assignment of **1**, **3** and **4**.

Compound / Carbon	**1**(CD_3OD)	**3**[2] (D_2O)	**4**[2] (D_2O)
1	95.1 d J=178*	94.5 d J=176	93.8
3	162.4 d J=191*	152.6 d J=196	139.4
4	126.9 s	114.3 s	119.1
5	68.2 s	68.7	70.1
6	44.5† t	45.9 t J=135	43.3
7	80.4 d J=152	77.2	76.8
8	78.6 s	79.1	79.2
9	58.1 d J=135	56.9 d J=132	58.0
10	21.4 q J=125	20.6 q J=129	21.3
11	192.5 d J=175	168.9	59.7
		52.6	
1'	99.8 d J=162	99.2 d J=165	99.8
2'	74.3 d J=144	73.3	73.4
3'	78.2 d J=144	76.2	76.3
4'	71.5 d J=144	70.4	70.6
5'	77.3 d J=144	77.2	77.1
6'	62.7 t J=147	61.5 t J=145	61.6
C=O	168.1 s		
CH	146.5 d J=155		
CH	119.0 d J=160		
1''	135.7		
2''	129.9		
3''	129.2		
4''	131.4		
5''	129.2		
6''	129.9		

Standard used were TMS for **1** and Dioxane (67.4 ppm from TMS) for **3** and **4**. Chemical shifts in ppm±0.1. Coupling constants in Hz ±2. Asterisk indicates a non measurable additional coupling constant. Values with the same superscript in the vertical column are interchangeable.

†Partially superimposed to CD_3OD signals.

deshielding of two primary and three secondary protons geminal with oxygenated functions. The ^{13}C-nmr spectrum of **1** (PND and SFORD, see table) further confirmed the iridoidic structure. The presence of the aldehydic group (192.5 ppm) at C–11 is confirmed by the deshielding of the C–3 (162.4 ppm) and C–4 (126.9 ppm) carbons. That of two tertiary hydroxyl groups at C–5 and C–8 is supported by the singlets at 68.2 and 78.6 ppm, respectively. The lack of α and β esterification effects on glucosylic carbons proved that the cinnamoyl residue esterified a secondary (see above) alcoholic function of the aglycone. One of the most interesting data of the ^{13}C-nmr spectrum of **1** was the chemical shift value (21.4 ppm) of the C–10 methyl group. In fact, it is very close to that found in lamiide (**3**) (20.6 ppm), lamiidol (**4**) (21.3 ppm) and phlomiol (21.0 ppm)[1] (2), all with an α methyl group at C–10 and a β vicinal diol function at C–7 and C–8. In daunoside, which has the same configuration of the C–8 centre but an α hydroxyl function at C–7, the methyl group signal falls at 15.9 ppm (3). In ipolamiide, which differs from lamiide only in the lack of the secondary alcoholic function at C–7, the C–10 resonates at 22.8 ppm (2), while at 23.8 ppm in lamiol (2) and at 24.7 ppm in harpagide (2) both having the β secondary alcoholic function at C–6.

By considering on one hand **3**, **4** and phlomiol, and on the other hand ipolamiide, lamiol and harpagide, the differences of the chemical shift values of the C–10 can be explained on the basis of the presence in all compounds of the first group of a γ shielding effect owing to the β secondary hydroxyl function at C–7.

Therefore, also in **1** the secondary alcoholic function on the cyclopentane ring

[1]These spectra have been recorded in D_2O, but the solvent effects in this case can be neglected as it results from spectra of similar iridoid glucosides recorded both in D_2O or in CD_3OD.

must be at C-7 and in β configuration, that is the same as saying, that **1** differs from **3** only in the substituent at C-4 and in the esterification of the OH-7 by the *trans* cinnamic acid.

In accordance, the chemical shift of the methylene group (2.33 ppm) in the ^{1}H-nmr spectrum of **1** is very similar to that (2.29 ppm) of lamiide (**3**) (4); on the contrary the chemical shift of the methylene at C-7 of lamioside (8-O-acetyllamiol) appears more shielded even if it is vicinal to the ester function at C-8.

In order to obtain a conclusive determination of structure and configuration of **1**, we treated it with $NaBH_4$. The successive alkaline hydrolysis afforded a compound identical (^{1}H-nmr, ^{13}C-nmr, see exprimental) to lamiidol (**4**) (4), prepared previously by $LiAlH_4$ reduction of lamiide pentaacetate (4).

In addition, it is found by comparison of the ^{13}C-nmr spectra of **1**, **3** and **4**: *i*) the chemical shift of C-5 is very similar in **1** (68.2 ppm) and **3** (68.7 ppm) while it is larger in **4** (70.1 ppm); *ii*) the aldehydic group at C-11 causes a deshielding of C-3 and C-4 larger than those caused by the $COOCH_3$, in fact these carbons resonate at 162.4 and 126.9 ppm in **1** and at 152.5 and 114.3 ppm, respectively, in **3**; *iii*) the esterification effects on α and β carbons are very small and sometimes can be obscured by effects of conformational changes caused by the presence of different substituents on remote carbons, i.e., the α and β effects can be observed in the comparison between the spectra of **1** and **3**, in fact in **1** C-7, C-6 and C-8 carbons resonate at 80.4, 44.5 and 78.6 ppm, respectively, while in **3** at 77.2, 45.9 and 79.1 ppm; on the contrary in the comparison between the spectra of **1** and **4**, the C-6 carbon appears more shielded in **4** (C-7 76.8, C-6 43.3, C-8 79.2 ppm) than in **1**.

EXPERIMENTAL[2]

ISOLATION OF IRIDOID-CONTAINING FRACTION.—*Pondranea ricasoliana* (Tauf) Sprague (Bignoniaceae) was collected in September 1980 near Puerto de la Cruz, Tenerife, Canary Islands, when it was in flower. Voucher specimens of the plant were identified by Dr. Anna Francesconi, Istituto di Botanica dell'Università di Roma. Fresh aerial parts of the plant (0.5 kg) were extracted with 90% EtOH (1.2 lx3) at room temperature for 5 days. Paper chromatography with *n*-butanol-acetic acid-water (63:10:27) showed the presence of two iridoids with Rf values 0.63 for pondraneoside (**1**), and 0.72 for iridoid A.

The ethanolic extract was concentrated to an aqueous suspension which was treated with decolorizing charcoal (100 g). The resulting suspension was stratified on a gooch funnel (10 cm ∅); monosaccharides were eluted with water (3 liters), disaccharides with 5% ethanol (1 liter) and 10% ethanol (1 liter); traces of iridoid-like compounds with 30% ethanol (2 liters), **1** and A with 50% ethanol (0.5 liter) and 80% ethanol (3 liters): the resulting dried extract (6.0 g) was chromatographed on Si gel (600 g) in chloroform-methanol (8:2) to give A (0.4 g) and **1** (0.6 g), both as crude products. When **1** was rechromatographed on Si gel (60 g) in the above eluent pure **1** (0.4 g) was obtained as an amorphous powder. It exhibited the following data: $[\alpha]^{25}D = -69.2°$ (MeOH, c 3.2); uv λ max (MeOH) nm (log ϵ): 222 (4.3), 243 (4.3), 277 (4.3); ir ν max (KBr) cm^{-1} 2730(s), 1720(s), 1685, 1655, 1650, 1635; ^{1}H-nmr (90 MHz, D_2O): 9.05(H-11,s), 7.60(CH-β,d,J=16 Hz), 7.7-7.2(H-3) covered by aromatic signals), 6.47(CH-α,d,J=16 Hz), 5.85(H-1,s), 4.70(H-7 superimposed to H-1'), 2.82(H-9,s), 2.33(2H-6,bsg), 1.09(3H-10,s) ppm.

ALKALINE HYDROLYSIS OF **1**.—Compound **1** (50 mg) was treated with 2 ml of 2N NaOH for 12 hr at room temperature. The solution was acidified and extracted with ether (15 ml x 3). It gave a compound (15 mg) found to be identical to *trans* cinnamic acid by comparison of the ^{1}H-nmr and uv spectra.

TETRAACETATE OF **1**:**2**.—Compound **1** (40 mg) was treated with dry pyridine (0.5 ml) and Ac_2O (1.0 ml) for 1 hr at room temperature. After the addition of methanol (3.0 ml), the solution was left for 20 min then evaporated to give crude **2** (70 mg) which was chromatographed on Si gel (7 g) in ether-ethyl acetate (7:3) to give pure **2** (50 mg). It crystallized from 95% ethanol as needles: mp 227-227.5°; ^{1}H-nmr (90 MHz, $CDCl_3$): 9.37 (H-11,s), 7.71(CH-β,d,J=16 Hz), 7.08 (H-3,s), 6.57 (CH-α,d,J=16 Hz), 5.78(H-1,s), 4.8-5.3(H-7), 2.93(H-9,s), 2.46 (2H-6,m), 1.21(3H-10,s) ppm. Elem. anal. (calcd. for $C_{33}H_{38}O_{16}$): C% 57.24 (57.41), H% 5.72 (5.51).

$NaBH_4$ REDUCTION OF **1** AND SUCCESSIVE ALKALINE HYDROLYSIS, LAMIIDOL (**4**).—Compound **1** (60 mg) dissolved in water (5 ml) was treated with $NaBH_4$ for 4 hr at room temperature.

[2]Pc: Schleicher & Schull No. 2043 b Mgl. Tlc: Merck Silica gel plates Kieselgel 60 F_{254}. Spray reagents: Vanillin (2 g vanillin, 4 ml conc HCl, 100 ml MeOH) for pc, 2N H_2SO_4 for tlc by heating at 100° for 3 min. Evaporation of volatile materials was performed under reduced pressure.

The excess hydride was destroyed by bubbling CO_2 until pH 7 was attained and 15% NaOH (4 ml) was then added. The solution was left for 24 hr at room temperature, then neutralized by bubbling CO_2 and treated with decolorizing charcoal (1 g). The resulting suspension was stratified on a gooch funnel (2 cm ∅); the carbon layer was washed with water (0.5 l) to remove salts, then eluted with methanol (100 ml). The solution ,when evaporated, gave 20 mg of a compound which was identical to lamiidol (**4**).

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