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PHENYLPROPANOID GLYCOSIDES FROM *MUSSATIA HYACINTHINA*

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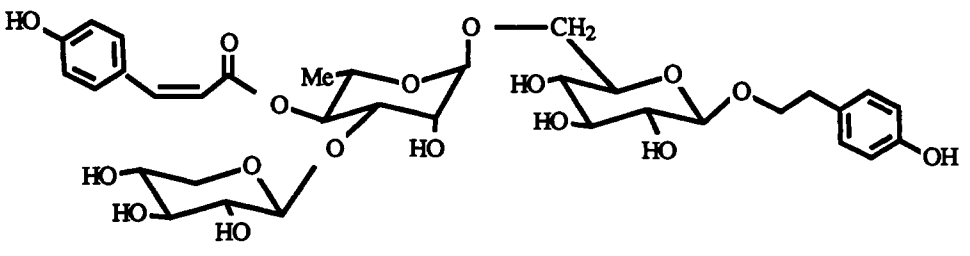
ABSTRACT.—A new phenylpropanoid glycoside, 4-*cis*-*p*-coumaroyl mussatioside [**1**], was isolated from the bark of *Mussatia hyacinthina*, along with the already known, mussatioside, 4-vanilloyl mussatioside, 4-*trans*-*p*-coumaroyl mussatioside, 4-feruoyl mussatioside, 4-dimethyl caffeoyl mussatioside, 4-cinnamoyl mussatioside, 4-*p*-methoxycinnamoyl mussatioside and 4-cinnamoyl desxylosyl mussatioside. Compound **1** was also isolated from *Mussatia* sp. nov, and this indicates that both species are very closely related botanically.

As a continuation of our studies with members of the Bignoniaceae, we became interested in the genus *Mussatia* with two species, *Mussatia hyacinthina* (Standl.) Sandw. and *Mussatia prieurei* (DC.) Bur. ex K. Schum., widely distributed in South America.

In previous papers (1,2) we reported the isolation of eight new phenylpropanoid glycosides from *Mussatia* sp. nov., a new species from Peru. In this communication we describe our results on *M. hyacinthina* from Bolivia. Both species are known locally as "chamairo" and are chewed alone or mixed with coca leaves for sweetening, euphoric, or medicinal effects (3–5). Although Gentry, in his work on the American Bignoniaceae, has studied both species and distinguished them by the anatomy of the leaf surface, a definite botanical description of the third new *Mussatia* species has not yet been published (4). The results we report here contribute to our understanding of the "chamairo" complex.

Bark of *M. hyacinthina* (blanco form) was defatted with hexane and the residue extracted with MeOH and condensed. The MeOH extract, which was fractionated following the published procedure (2), gave nine phenylpropanoid glycosides: mussatioside, 4-vanilloyl mussatioside, 4-*trans*-*p*-coumaroyl mussatioside, 4-feruloyl mussatioside, 4-dimethylcaffeoyl mussatioside, 4-cinnamoyl mussatioside, 4-*p*-methoxycinnamoyl mussatioside, 4-cinnamoyl desxylosyl mussatioside, and 4-*cis*-*p*-coumaroyl mussatioside [**1**]. Compound **1** is a new natural product whose structure was deduced on the basis of spectral data in comparison with the other phenylpropanoid glycosides.

4-*cis*-*p*-Coumaroyl mussatioside [**1**] was isolated as an amorphous powder. Ion peaks at *m/z* $[M+Na]^+$ 747 and $[M-H+2Na]^+$ 768 in the fabms, ob-



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tained on addition of NaCl, indicated the molecular formula $C_{34}H_{44}O_{17}$. The ^{1}H-nmr spectrum of **1** was very similar to that of 4-*trans*-*p*-coumaroyl mussatioside, the main difference being the signals of the protons attached to the α and β carbons of the *p*-coumaric acid residue. In the *cis* compound, the olefinic protons appeared as doublets (J = 12.8 Hz) at δ 6.94 and 5.75 while in the *trans* isomer they resonated at δ 7.60 and 6.30 (J = 16.0 Hz). In addition, the H-2″, -6″ and H-3″, -5″ aromatic protons appeared downfield in the *cis* compound **1** (δ 7.73 and 6.82) as compared to the *trans* isomer (δ 7.42 and 6.78). Chemical shifts and J values were in good agreement with those described in the literature for other *cis*/*trans* phenylpropanoid glycosides (6). Homonuclear ^{1}H-^{1}H correlation (COSY) was used to confirm these assignments.

These data indicate that compound **1** is β-(4′-hydroxyphenyl)-ethyl-*O*-β-D-xylopyranosyl (1↦3)-*O*-(4-*O*-*cis*-*p*-coumaroyl-α-L-rhamnopyranosil)-(1↦6)-*O*-β-D-glucopyranoside.

In order to obtain more information on the chamairo complex, we carried out a further study on the composition of the already reported *Mussatia* sp. nov. In addition to the eight glycosides already reported, the phenylpropanoid glycoside **1** was also found as a minor component of the bark. Thus, both *M. hyacinthina* and the new species have an identical chemical composition, and this can be interpreted as a chemotaxonomic indication that they are very closely related botanically.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—^{1}H-nmr spectra (250 MHz) were recorded on a Bruker WM-250; rotation locular countercurrent chromatography (rlcc) was performed on a Tokyo Rikakikai Co. apparatus and hplc separations on Whatman Partisil ODS and μ-Bondapak NH_2 columns using a Waters Associates Model 590 chromatograph, equipped with a uv detector operated at 254 nm and R401 differential refractometer; the fabms spectrum was performed with a Kratos MS-50 apparatus.

PLANT MATERIAL.—The plant material was purchased by E.W. Davis in the Rurrenabaque market in the province of Caupolican, Department of La Paz, Bolivia, and identified by A. Gentry as *M. hyacinthina* (blanco form). A voucher specimen (Davis Collection, No. 1206) is deposited at Harvard University.

ISOLATION PROCEDURES.—The bark (372 g) of *M. hyacinthina* was defatted with hexane and the residue extracted with MeOH and condensed to give 66 g of MeOH extract. Part of this extract (15 g) was fractionated as described previously (2) to give the already known phenylpropanoid glycosides: mussatioside (53 mg), 4-vanilloyl mussatioside (20 mg), 4-*trans*-*p*-coumaroyl mussatioside (29 mg), 4-feruloyl mussatioside (13 mg), 4-dimethylcaffeoyl mussatioside (132 mg), 4-cinnamoyl mussatioside (290 mg), 4-*p*-methoxycinnamoyl mussatioside (17 mg), 4-cinnamoyl desxylosyl mussatioside (3 mg), and the new 4-*cis*-*p*-coumaroyl mussatioside [**1**] (4 mg). Compound **1** was eluted in the rlcc in the first fraction together with the first four compounds and was further purified by hplc [μ-Bondapak NH_2, MeCN-H_2O (86:14), flow 2 ml/min, Rt 36 min].

4-*cis*-*p*-COUMAROYL MUSSATIOSIDE [**1**].—An amorphous powder, $[\alpha]^{25}D$ −19.6° (MeOH, c = 0.20); ^{1}H nmr (250 MHz, CD_3OD) aglycone moiety δ 2.91 (2H, t, J = 6.6 Hz, H-7′), 3.60 (1H, m, H-8′), 3.95 (1H, m, H-8′), 6.77 (2H, d, J = 8.5 Hz, H-3′, H-5′), 7.14 (2H, d, J = 8.5 Hz, H-2′, H-6′); glucose moiety δ 4.33 (1H, d, J = 7.8 Hz, H-1), 3.20 (1H, dd, J = 7.8, 9.0 Hz, H-2); rhamnose moiety δ 4.85 (1H, d, J = 1.5 Hz, H-1), 5.19 (1H, t, J = 9.7 Hz, H-4), 1.21 (3H, d, J = 6.3 Hz, 5-Me); xylose moiety δ 4.36 (1H, d, J = 7.8 Hz, H-1), 3.10 (1H, dd, J = 7.0, 3.0 Hz, H-2); *cis*-*p*-coumaroyl moiety δ 5.75 (1H, d, J = 12.8 Hz, H-8″), 6.82 (2H, d, J = 8.8 Hz, H-3″, H-5″), 6.94 (1H, d, J = 12.8 Hz, H-7′), 7.73 (2H, d, J = 8.8 Hz, H-2″, H-6″); fabms *m/z* (rel. int.) $[M+Na]^+$ 747 (100), $[M-H+2Na]^+$ 768 (29).

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