

CHEMICAL CONSTITUENTS OF *LYTHOSPERMUM FRUTICOSUM*

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Lithospermum fruticosum L. belongs to the family Boraginaceae and is used in folk medicine to treat high blood pressure. Although different papers (1-5) have reported compounds isolated from other species of the same genus, there are no reported analyses of *L. fruticosum*. We made an analysis of hexane and alcoholic extracts of this plant, and we wish now to report the compounds isolated and identified. The plant was collected in October 1980, at Simar de Valldigna (Valencia, Spain) and classified by Dr. Mansanet, Professor of Botany, University of Valencia. Leaves and stems of the plant (8 kg) were successively and exhaustively extracted with hexane and EtOH in a Soxhlet extractor. The hexane (450 g, 5.6% of dry plant) and the ethanolic (800 g, 10% of dry plant) extracts were separated into neutral and acidic fractions. Column chromatography of neutral fractions and of methyl esters of acidic fractions on silica gel allowed us to isolate and identify the compounds in Table I (7-19).

TABLE I. Compounds Isolated and Identified from Hexane and Ethanolic Extracts of the *Lithospermum fruticosum*

Class of compound (reference)	Percentage related to H (Hexane) or A (alcoholic) extract	Main Components or single compound properties (relative %)	Identified by
Saturated π -hydrocarbons	0.39 H	C ₂₅ (8), C ₂₇ (28), C ₂₉ (23), C ₃₁ (15)	ir, gc
Wax esters	5.5 H	1-Alkanols C ₂₀ (12), C ₂₂ (5), C ₂₄ (27), C ₂₆ (21) Sat. alkanolic acids C ₁₆ (17), C ₁₈ (7), C ₂₀ (46), C ₂₂ (15), C ₂₄ (13.5)	hydrolysis: ir, gc of acetates ir, gc of methyl esters
Free 1-alkanols	2.0 H	C ₃₀ (54.7), C ₂₈ (35.5), C ₂₆ (7.7)	ir, gc of acetates
Free aliphatic acids	0.3 H	C ₁₈ (41), C ₁₈ (16), C ₁₆ (16), C ₁₆ (14.3)	ir, gc of methyl esters
Triterpenols (7-9)	6.2 H	β -Amyrin (67) Lupeol (33)	ir, gc of acetate pmr, ms
Phytosterols (10, 11)	10.0 H	β -Sitosterol (79) Campesterol (12.5) Stigmasterol (1.5)	ir, pmr, gc of TMS-ethers
Phytosterol glucosides (10, 11)	0.5 A	Aglucosides: β -sitosterol (79.5) campesterol (7.7), stigmasterol (0.75) and unknown (12)	ir, pmr, ms, hydrolysis gc of TMS-ethers
Bornesitol (12-14)	7.5 A	Sugar: glucose (89.2) C ₇ H ₁₄ O ₆ ; mp 200-202 [α] _D -32	gc of TMS-ethers ir, pmr, rotation, ms; pentaacetate mp 138-139° and its pmr; mesoinositol mp 224-225° (HI demethylation)
Syringin (15, 16)	9.0 A	C ₁₇ H ₂₄ O ₉ ; mp 192-194° [α] _D -17.5	ir, pmr, uv, rotation; pentaacetylsyringin mp 105-106° and its ir, pmr dihydrosyringin mp 149-150°
Sinapylaldehyde glucoside (17)	0.035 A	C ₁₇ H ₂₂ O ₉ ; mp 221-222° glucose (hydrolysis)	ir, pmr, ms, partial synthesis from syringin gc of TMS-ether
Rutin (18)	0.003 A	C ₂₇ H ₃₀ O ₁₆ ; mp 214° dec. Quercetin (by hydrolysis) glucose and rhamnose	ir, pmr, uv and its shifts ir, pmr, uv and its shifts, mp 313-315° gc of TMS-ethers
Coniferyl alcohol (19)	0.006 A	C ₁₀ H ₁₂ O ₃ ; mp 73-75	ir, pmr, uv, ms, diacetate: ir, pmr, ms

The best procedure to isolate bornesitol, sinapylaldehyde glucoside, and syringin was as follows. The crude alcoholic extract was chromatographed on a column of charcoal and celite; cold H₂O eluted from the column crystalline bornesitol (on reduction of the volume) and sugars. Treatment of the column material with phenol-saturated H₂O recovered other components, which were further separated by column chromatography on polyamide (0 S-6 Macherey Nagel); elution with H₂O gave two glucosides and with MeOH-H₂O (60:40) gave rutin (6). The glucosides, syringin and sinapylaldehyde glucoside, were separated from each other by chromatography on kiesel gel 60 Merck (70-200 mesh); CH₂Cl₂-MeOH (8:1) eluted sinapylaldehyde glucoside and CH₂Cl₂-MeOH (6:1) eluted syringin. Sinapylaldehyde glucoside has been previously isolated from *Fraxinus griffithii* (17).

Full details of the isolation and identification of the compounds are available on request to the senior author.

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ESSENTIAL OILS OF SOME AMAZONIAN LABIATAE, 1. GENUS *HYPTIS*

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The genus *Hyptis* (Labiatae) is composed of 400 species that occur in tropical America (1). Many of these plants are quite aromatic and are reported to possess medicinal properties (2, 3). Several species of *Hyptis* have been found to possess significant pharmacological activities (4, 5).

Essential oils from aerial parts of some species of the genus *Hyptis* were reported earlier (6-8). In this report, we present the chemical constituents of the essential oils from four species of *Hyptis* occurring in the Amazon (Table 1). Two of these, *Hyptis suaveolens* Poit. and *Hyptis goyazensis* Benth., were studied by us previously (9). Now, in addition, many other terpenoid constituents are reported.

TABLE 1. Essential Oils of *Hyptis* Species: Collection Data and Yields

Ref. No.	Common Name	Species	Origin	Oil Yield %
020A	Mentrasito	<i>H. suaveolens</i>	Aripuanã, MT ^a	0.6
21A	Alfavacão	<i>H. mutabilis</i>	Aripuanã, MT	0.3
M-76	Alfavacão	<i>H. mutabilis</i>	Taciateua, PA ^b	0.4
M-24	Estoraque	<i>H. spp.</i>	Bujaru, PA	0.2
M-46	Romaninho	<i>H. goyazensis</i>	S. Caetano, PA	0.6

^aMato Grosso.

^bPará.

DISCUSSION

Identification of many of the components was accomplished by comparison of mass spectra and gas chromatographic retention data of authentic compounds. Remaining components were identified by comparison of their mass spectra to those in the data system library and in the literature. Peaks whose identities were confirmed by comparison of their spectra and their gc retention data with those of authentic compounds are so indicated. α -Pinene, myrcene, and β -caryophyllene are the only constituents present in all species studied (Table 2). 1,8-Cineole and β -caryophyllene are the same principal components in the oils of