

The alcoholic extract (53.5 g) was divided into two equal parts. The first half was fractionated over silica gel (800 g) using CHCl_3 -MeOH mixtures, to give: quercetrin (55 mg, mp 250-252°, mmp no depression), kaempferol-3-*O*-rhamnoside (23 mg, mp 172-175°; uv λ max 269, 290 sh, 350 nm), kaempferol-3-*O*-rhamnoglucoside (62 mg, mp 222-223°; uv λ max 268, 290 sh, 349 nm; acid hydrolysis yielded kaempferol, rhamnose, and glucose), rutin (75 mg, mp 189-192°, mixed mp no depression) and mannitol (1.85 g, mp 166-168°, mixed mp no depression, M^+ 182).

The second half of the alcoholic extract was chromatographed over alumina (1 kg). Fractions eluted by CHCl_3 -MeOH mixtures 9:1, 8:2, and 7:3 showed five pink spots by silica gel tlc (CHCl_3 -MeOH 82:18; H_2SO_4 visualization). Further fractionation over silica gel (200 g) gave three iridoids: jasminin glucoside (180 mg, mp 158-159°, mmp no depression), sambacin glucoside (52 mg, mp 150-153°, recently isolated by us for the first time from *Jasminum sambac* Ait. (7), and an as yet uncharacterized compound (200 mg, mp 146-148°, uv λ max 262 nm, M^+ 364), provisionally termed azoricin upon which work is in progress to identify its structure.

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LITERATURE CITED

1. L.H. Bailey, "The Standard Cyclopedia of Horticulture," vol. 2. New York: MacMillan, 1963, p. 1718.
2. R.N. Chopra, "Indigenous Drugs of India," Calcutta: Dhur and Sons, Private Ltd., 2nd ed., 1958, p. 64.
3. T. Kamikawa, K. Inoue, and T. Kubota, *Tetrahedron*, **26**, 4561 (1970).
4. H.M. Pousrat, T. Le-Men, and N. Boustany, *Ann. Pharm. Franc.*, **12**, 59 (1959).
5. N.K. Hart, S.R. Johns, J.A. Lamberton, *Aust. J. Chem.*, **22**, 1283 (1969).
6. A.M. El-Moghazy, A.A. Ali, S.A. Ross, A.A. Mohamed, *Fitoterapia*, **4**, 197 (1980).
7. S.A. Ross, S.M. El-Sayyad, A.A. Ali, N.E. El-Keltawy, *Fitoterapia*, **3**, 91 (1982).
8. N.K. Hart, S.R. Johns, J.A. Lamberton, *Aust. J. Chem.*, **21**, 1321 (1968).
9. A.R. Johnson, J.B. Davenport, "Biochemistry and Methodology of Lipids," New York: Wiley Interscience, 1971, p. 35.
10. T.J. Mabry, K.R. Markham, and M.B. Thomas, "The Systematic Identification of Flavonoids," New York: Springer-Verlag, 1970.
11. J.B. Harborne, "Comparative Biochemistry of the Flavonoids," London: Academic Press, 1967.

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CINNAMIC ACID ESTERS FROM *MEUM ATHAMANTICUM*

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Meum athamanticum Jacq. (Umbelliferae) is an herbaceous plant, widespread in the western and central European mountains. Aqueous and methanolic extracts of the rhizome show a platelet anti-aggregant activity *in vitro* (1). Part of the activity is associated (1) with the presence of methyl esters of 1-caffeoyl and 1-feruloyl quinic acids (2) in the methanolic extract. We wish to report here the purification and identification of four additional cinnamic acid esters from the rhizome of *M. athamanticum*. From the aqueous extract, 2.3 mg of methyl ferulate (4-hydroxy-3-methoxy cinnamic acid methyl ester), 4 mg of methyl caffeate (3,4-dihydroxycinnamic acid methyl ester), and 80 mg of malonic acid were isolated; 2.4 mg of caffeoyl quinic acid (3,4-dihydroxy cinnamoyl quinic acid) and 2 mg of feruloyl quinic acid (4-hydroxy-3-methoxy cinnamoyl quinic acid) were separated from the methanolic extract. All compounds were identified by uv, ir, pmr, and/or ms. Both caffeoyl quinic and malonic acids co-chromatographed with reference samples on tlc; however, the spectral data obtained did not permit the location of the position of acylation of the quinyll moiety in either feruloyl quinic or caffeoyl quinic acids. Methyl ferulate and particularly methyl caffeate showed a significant platelet anti-aggregant activity *in vitro*.

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

EXPERIMENTAL

PLANT MATERIAL.—*M. atbamanticum* rhizomes (1180 g) were collected from Col du Lautaret, France, at the beginning of the fruiting stage. Samples have been deposited at the Laboratoire de Pharmacognosie, UER de Pharmacie de Grenoble.

EXTRACTION OF THE PLANT MATERIAL.—The powdered rhizome tissue was successively extracted with hexane, CHCl_3 , and MeOH. The residual material was boiled in H_2O for 1 h, and the aqueous extract was immediately lyophilized.

LITERATURE CITED

1. D. Barron, L. Kolodie, and A.M. Mariotte, *Plant. Med. Phytother.*, **17**, 107 (1983).
2. D. Barron, M. Kaouadji, and A.M. Mariotte, *Z. Naturforsch.*, **39c**, 167 (1984).

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TERPENOIDS OF *MONARDELLA HYPOLEUCA*

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Monardella hypoleuca Gray (Lamiaceae) is a suffrutescent perennial found on dry canyon slopes of southern California. A decoction of the plant has been used by the Western Indian tribes as an expectorant, stimulant, and an aid to digestion (1, 2). Our investigations have centered around species of the mint family that may have some pharmacological activity and were carried out in the hope of obtaining information that would be of value in systematic plant identification. This communication is the first in a series on the terpenoid constituents of the genus *Monardella*.

We have identified 12 terpenoid constituents by gc and gc/ms. The compounds identified and their relative percentages were: piperitone (0.2%), β -caryophyllene (0.7%), piperitenone (1.3%), α -thujene (3.4%), 1,8-cineole (4.3%), Δ -3-carene (8.7%), and *trans*- β -farnesene (76.0%). Other trace components were β -pinene, camphor, isoborneol, δ -cadinene, and an unidentified caryophyllene isomer. The presence of Δ -3-carene is of interest in that it has been found in *Lepichinia calycina* (3).

EXPERIMENTAL

PLANT MATERIALS.—Plants were collected by S.A.J. in Santa Barbara County, California. A voucher specimen is deposited in the Santa Barbara Botanic Garden Herbarium.

EXTRACTION AND ANALYSIS.—Three separate isolation techniques were performed: steam distillation using a modified Clevenger apparatus, distillation using a Likens-Nikerson apparatus, and solvent extraction (4). Relative percentages of components were slightly higher for oxygenated monoterpenoids and sesquiterpenoids but were within one standard deviation of the values reported here in five trial runs using solvent extraction. Solvent extraction was performed by grinding 25 g fresh leaves in a mortar and pestle with two successive washings of 100 ml each of *n*-pentane-Et₂O (2:1, v/v) and dry ice. The solution was filtered through glass wool over Na₂SO₄ and concentrated to dryness under N₂ in an ice bath. The residue was resolvated with 3 ml of hexane (boiling point, 68.5–69.4°) and refiltered with 0.5 μm Millipore Syringe filter equipped with a Swinney adaptor. The solution was analyzed immediately by gc and gc/ms. Two gas chromatographs equipped with flame ionization detectors were used. A Hewlett-Packard model 5831A gc was equipped with two columns, 3% SE-30 on Chromosorb WHP 80/100 (2 mm \times 1.8 m glass column) and 3% OV-17 on Chromosorb WHP 100/120 HAW DCMS (2 mm \times 1.8 m glass column). Analysis was done by temperature programming from 100–270°, 1.0 min initial hold, 10°/min, 5.0 min final hold. The carrier gas was Helium at 27 ml/min. A Hewlett-Packard model 5840 gc equipped with a