Flavones From Some Canary Species of Sideritis

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From species of the genus Sideritis (Labiatae) endemic to the Canary Islands, several new diterpenes (1, 2) were previously obtained together with the coumarin siderin (3). The present work reports the isolation of flavones from several species of Sideritis.

From Sideritis bolleana Bornm., a species endemic to San Miguel de La Palma, 3,7,4'-tri-O-methyl-kaempferol (4) was obtained; from S. dasynaphala (Webb) Clos., endemic to Gran Canaria, cirsimaritin (5) and xanthomicrol (6) were isolated. S. gomerae Bolle proved to be the species richest in flavones: 3,7,4'-tri-O-methyl-kaempferol, 5-hydroxy-7,4'-dimethoxy-flavone (3,4'-di-O-methyl-apigenin) (7a), 5-hydroxy-3,6,7,4'-tetramethoxy-flavone (3,4'-di-O-methyl-eupalitin) (8, 9), 5-hydroxy-6,7,4'-trimethoxy-flavone (salvigenin) (10), 5,7-dihydroxy-6,4'-dimethoxy-flavone (pectolinarigenin) (11), 5-hydroxy-3,6,7,3',4'-pentamethoxy-flavone (artemetin) (7b), 5-hydroxy-6,7,3',4'-tetramethoxy-flavone (3'-O-methyl-eupatorin) (12), and 5,3'-dihydroxy-6,7,4'-trimethoxy-flavone (eupatorin) (11) were obtained from this plant.

No flavones were isolated from Sideritis canariensis L., S. macrostachya Poir, S. argophacelus (Webb) Clos, S. dendrochahorra Bolle, S. soluta Clos or S. candicans Ait. which were collected during the same season. This fact could be significant from the phytotaxonomical standpoint in view of the difficulty involved in assigning some of these species an accurate botanical classification (13).

EXPERIMENTAL

Isolation of flavones.—The air-dried aerial part of the plant was chopped and extracted several times with EtOH in a Soxhlet. The cold extract was filtered, concentrated a vacuo and chromatographed on a column over silica gel. Petroleum ether, petroleum ether-ETAC and EtOAc were used to elute mixtures of terpenoids, sterols and flavones. These latter were separated by re-chromatography on dry-column silica gel.

Collection of S. bolleana.—S. bolleana (4.5 kg) was collected on La Palma (island) near Fuencaliente beside the south road at km 27. The plant yielded the following:

5-HYDROXY-3,7,4'-TRIMETHOXY-FLAVONE (3,7,4'-TRI-O-METHYL-KAEMPFEROL) (60 mg).
—The mp was 147–149° (petroleum ether-EtOAc) lit. 154–155°. UV λ max (MeOH) nm 269, 333, λ max (MeOH+MeONa) 285, 360. NMR 3.84 (9H, s), 6.39, 6.41 (1H each, d, J = 2.5 Hz), 7.00, 8.07 (2H each, d, J = 9 Hz) and 12.64 (1H, s).

Collection of S. dasynaphala.—S. dasynaphala (1.5 kg) was collected in Tejeda (Gran Canaria) at 1700 m altitude. The constituents isolated from S. dasynaphala are given below along with their physical data.

5,4'-DIHYDROXY-6,7-DIMETHOXY-FLAVONE (CIRSIMARITIN) (50 mg).—The mp was 273–274° (petroleum ether-ETAC 5%) lit. (5) 263–265°. UV λ max (EtOH) nm 277, 336, λ max (EtOH+AlCl₃) 265, 287, 303, 359. Diacetate: NMR 3.30 (3H, s), 3.45 (3H, s), 3.83 (3H, s), 3.98 (3H, s) 6.59 (1H, s), 6.90 (1H, s), 7.27 and 7.88 (2H each, d, J = 9 Hz). By methylation of the compound with diazomethane (0°, 2h), salvigenin was obtained.

5,4'-DIHYDROXY-6,7,8-TRIMETHOXY-FLAVONE (XANTHOMICROL) (70 mg).—The mp was 225–227° (petroleum ether-ETOAc 5%) lit. (6) 228°. UV λ max (EtOH) nm 282, 292, 334, λ max (EtOH+AlCl₃) 287, 312, 353. NMR (CCl₃) 3.92 (6H, s), 4.08 (3H, s), 6.58 (1H, s), 6.93 and 7.82 (2H each, d, J = 9 Hz).

Collection of S. gomerae.—S. gomerae (2 kg) collected on the island of La Gomera


2Mp's are uncorrected. NMR spectra were taken in CDCl₃ with TMS as internal reference, except where otherwise indicated.
at a point 4 km along the North Road contained the following substances:

5-HYDOXY-3,7,4',1'-TRIMETHOXY-FLAVONE (3, 7,4'-TRI-O-METHYL-KAEMPFEROL) (100 mg).—The 5-hydroxy-3,7,4',1'-trimethoxy-flavone was identical to that obtained from S. bolleana.

5-HYDOXY-7,4',1'-DIMETHOXY-FLAVONE (7,4'-DI-O-METHYL-APIGENIN) (190 mg).—The mp was 170–172° (petroleum ether-EtOAc 5%, lit. (7a) 174–174.5°. UV λ max (MeOH) nm 270, 329, λ max (EtOH+AlCl₃) 280, 303, 342, 382. NMR 3.88 (6H, s), 6.38, 6.40 (1H each, d, J=3 Hz), 6.59 (1H, s), 7.02, 7.38 (2H each, d, J=9 Hz) and 12.76 (1H, s).

5-HYDOXY-3,6,7,4',1'-TETRAMETHOXY-FLAVONE (3,4'-DI-O-METHYL-EUPALITIN) (130 mg).—The mp was 174–176° (petroleum ether-EtOAc 5%, lit. (8) 168–170°, lit (9) 169–171°. UV λ max (EtOH) nm 275, 338, λ max (EtOH+AlCl₃) 289, 362. NMR 3.86, 3.88, 3.91, 3.94 (3H each, s), 6.51 (1H, s), 7.03, 8.08 (2H each, d, J=9 Hz) and 12.61 (1H, s).

5-HYDOXY-6,7,4',1'-TRIMETHOXY-FLAVONE (SALVIGENIN) (160 mg).—The 5-hydroxy-6,7, 4',trimethoxy-flavone was identical to an authentic sample (10).

5,7-DIHYDROXY-6,4'-DIMETHOXY-FLAVONE (PECTOLINARIGENIN) (370 mg).—The physical constants and spectral data of 5,7-dihydroxy-6,4'-dimethoxy-flavone were identical to those reported in the literature (11).

5-HYDROXY-3,6,7,3',4'-PENTAMETHOXY-(ARTEMETIN) (50 mg).—The mp was 157–162° (petroleum ether), lit. (8) 159–160°, lit. (7b) 163–164°. NMR 3.91, 3.96 (3H each, s), 4.00 (9H, s), 6.57 (1H, s), 7.05, 7.80 (1H each, d, J=9 Hz), 7.73 (1H, s) and 12.55 (1H, s). MS (probe) 70 ev, m/e 388 (M⁺) 373 (M⁺-15), 322, 310, 308.

5-HYDROXY-6,7,3',4'-TETRAMETHOXY-FLAVONE (3'-O-METHYL-EUPATORIN) (60 mg).—The mp was 190–193° (MeOH), lit. (11) 190–191°. NMR 3.94 (3H, s), 3.98 (6H, s), 6.53 (1H, s), 6.62 (1H, s), 7.00, 7.54 (1H each, d, J=9 Hz), 7.38 (1H, s) and 12.73 (1H, s).

5,3'-DIHYDROXY-6,7,4',1'-TRIMETHOXY-FLAVONE (EUPATORIN) (180 mg).—The mp was 190–192° (petroleum ether-EtOAc), lit. (11) 196–198°. UV λ max (EtOH) nm 243, 254, 277, 343, λ max (EtOH+AlCl₃) 240, 264, 292, 370. NMR 3.94 (3H, s), 4.00 (6H, s), 6.53 (3H, s), 6.98, 7.48 (1H each, d, J=9 Hz), 7.33 (1H, s) and 12.62 (1H, s).

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