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COMPOSITAE

FLAVONOID AND TRITERPENE CONSTITUENTS OF *BACCHARIS RHOMBOIDALIS**

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DURING a current project dealing with Chilean flora,[1] we had occasion to examine *Baccharis rhomboidalis* Remy. The light petroleum extract of the dried pulverized plant yielded 5-hydroxy-7,4′-dimethoxyflavone, hentriacontanol, brein, and oleanolic acid. The benzene extract afforded acacetin; the ethanol extract showed a positive, but weak, alkaloid test.

EXPERIMENTAL

M.ps were determined on a Kofler block and are uncorrected. UV spectra were recorded on a Unicam SP 800 instrument and IR spectra on a Perkin–Elmer 457-B. The NMR spectra were determined on a Varian HA 100 instrument using $CDCl_3$ solutions with tetramethylsilane as internal reference. Merck silica gel GF_{254} was used for TLC. Light petroleum refers to the fraction of boiling range 65–75°.

Extraction. The dried, powdered leaves (8 kg) of *Baccharis rhomboidalis*, collected April 1966, at Tumbes, Concepcion, were extracted to exhaustion (Soxhlet) with light petroleum, benzene, and EtOH in turn.

Light petroleum extract. Concentration of this extract afforded a yellow semi-crystalline solid (110 g) and its mother liquors. The solid was collected and washed with EtOH. A portion of the solid (36 g) was chromatographed through alumina (grade I; 300 g) which had been treated with 4%, v/w dil. HOAc (1:9, HOAc–H_2O). The following compounds were eluted.

5-Hydroxy-7,4′-dimethoxyflavone (*I*). (8 g), eluted with light petroleum, m.p. (EtOH) 168° (lit. m.p. 173°),[2] ν_{max}^{KBr} 3400, 2850, 1620, 1500, 1440, 1350, 1250, 1190, 835, 770 cm^{-1}, λ_{max}^{EtOH} 270, 328 nm (ϵ 17,200, 19,680), NMR bands at τ 6·12 (6H, 2x MeO), 3 65 (1 Hd, *J* 3 Hz), 3 53 (1 Hd, *J* 3 Hz), 3·46 (1 Hs), 3·00, 2·18 (4 H, AA′BB′ pattern), −2·80 (1 Hs, exchanged with D_2O). (Calc. for $C_{17}H_{14}O_5$, C, 68 45; H, 4·75. Found: C, 68·46; H, 4·75%.)

On acetylation with Ac_2O in pyridine a monoacetate was formed, m.p. 196–198° (from EtOH), ν_{max}^{KBr} 2941, 2857, 1770, 1667, 1429, 1379, 1258 cm^{-1}, λ_{max}^{EtOH} 258, 275, 325 nm (ϵ 13,400, 8600, 27,800).

Further elution of the column with benzene–EtOH afforded a dark yellow solid, m p. 250–255° which was a metal complex of this flavone. Acetylation as above afforded an acetate identical to that from the free flavone. A sample of the complex was calcined to give an oxide which was melted with $K_2S_2O_7$. The residue in H_2O gave a + test for Al with morin, alizarin sulphonic acid and a blue colour to Thenard's test. Ca and Mg were absent. The same complex was formed when an aq. MeOH solution of the flavone (I) was treated with a solution of $Al_2(SO_4)_3$.

The EtOH solution obtained from washings of the solid (see above) was evaporated to give a dark yellow residue (65 g) which was treated with 2 N NaOH to give a 'neutral' fraction (45 g) and an acid extract (18 g). The latter was combined with the acid fraction from the petroleum extract mother liquors (see below).

The 'neutral' fraction (15 g) was chromatographed through alumina (grade I, 150 g) to give three components.

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Hentriacontanol (*II*). (0·1 g), eluted with benzene, m.p. (MeOH) 88–90° (lit. m.p. 85°),[3] $[\alpha]_D^{20}$ 0·00 (c 0·30, $CHCl_4$), ν_{max}^{film} 3333, 2941, 2857, 1709, 1471, 735, 724 cm^{-1}. Its mass spectrum showed M^+ at *m/e* 452. Its acetate had m.p. 75–77° (lit. m.p. 74–75°).[3] (Found: C, 80·71; H, 13·56. Calc. for $C_{33}H_{66}O_2$ C, 80·25; H, 13·46%.)

Brein (*III*). (75 mg) eluted with 1:99 EtOH–benzene, m.p. (EtOH) 200–202°, $[\alpha]_D^{20}$ +59° (c 0·5, $CHCl_3$) (lit. $[\alpha]_D$ +66°),[4] ν_{max}^{KBr} 3333, 2941, 1036, 1000, 675 cm^{-1}, NMR bands at τ 9·21 (6 Hs), 9·11 (3 Hs), 9·10 (3 Hs) 9·06 (3 Hs), 9·01 (6 Hs), 8·79 (3 Hs), 6·80 (1 Hdd, *J* 6, 9 Hz), 5·88 (1 Hdd, *J* 5·5, 11 Hz), 4·78 (1 Ht, *J* 3·5 Hz). Its mass spectrum showed bands at *m/e* 442 (M^+) (7), 234 (100), 219 (15), and 216 (20). (Found: C, 81·32; H, 11·29%.)

Acetylation as before afforded a diacetate, m.p. 185–189° (from EtOH) (lit. m.p. 196°),[4] $[\alpha]_D^{20}$ +74° (c 1·0, $CHCl_3$); the material was identical to an authentic sample by mixed m.p. and co-chromatography.

Oleanolic acid. 8·0 g, isolated by elution with benzene–EtOH, m.p. and mixed m.p. 305–307° (from EtOH). Its derived monoacetate had m.p. 261–263°, also undepressed on mixed m.p. with an authentic sample.

The remaining petroleum soluble extract was evaporated to dryness to afford a mixture (180 g) which was saponified with 5% NaOH in EtOH at reflux and then separated into acidic and neutral fractions. The acidic fraction was combined with the acidic material from above. TLC on this fraction (total weight 33 g) indicated the presence of the dimethoxyflavone (I), oleanolic acid, and some of the alcohol (II). This fraction was not further purified. A portion (15 g) of the neutral material (60 g) was chromatographed through alumina (grade I, 130 g). Elution with light petroleum gave a low melting hydrocarbon fraction. This was recrystallized from methanol several times to give m.p. 58–60° (80 mg), $[\alpha]_D^{20}$ 0·00 (c 0·3, $CHCl_3$), ν_{max}^{NaCl} 2985, 2874, 1473, 1361, 740, and 724 cm^{-1}, its mass spectrum showed no definite parent ion but was typical for a saturated fatty hydrocarbon.

Further elution of the column with light petroleum afforded more of the alcohol (II) (2 g) and brein (30 mg).

Benzene extract. Partial evaporation of this fraction afforded a crystalline precipitate (19·6 g). Repeated crystallization from EtOH gave *acacetin* (5,7-dihydroxy-4′-methoxyflavone) (IV) (6·8 g) as yellow needles, m.p. 250–260° (lit. m.p. 260°,,[5] ν_{max}^{KBr} 3279, 1669, 1608, 1597, 1590, 1379, 1354, 1299 cm^{-1}, λ_{max}^{EtOH} 210, 267, 325, 390 nm (ϵ 27,000, 15,250, 14,020, 8100), 6·15 (3 Hs), 3·50 (1 Hd, *J* 2·5 Hz), 3·59 (1 Hd, *J* 2·5 Hz), 3·00, 2·17 (4H, AA′BB′ system), −3·0 (2 Hs, exchanged by D_2O) (Calc. for $C_{20}H_{16}O_7$: C, 65·27; H, 4·38. Found: C, 65·27; H, 4·45%).

The mother liquor from the isolation of acacetin indicated only the presence of more oleanolic acid and flavone (I) and was not further purified. The remaining benzene soluble material (600 g), after saponification, contained oleanolic acid, acacetin, and the flavone (I).

Ethanol extract. Concentration of this solution afforded a semi-solid residue (700 g). A portion (138 g) of this fraction was extracted with 2·5 N HCl and the soluble portion was basified with excess NH_4OH. Extraction with EtOAc gave a small fraction which gave a faintly positive test for alkaloids. The presence of traces of alkaloids was further confirmed by paper chromatography, using Dragendorffs reagent as indicator. Since the quantity present was very small the alkaloids were not separated.

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