p-HYDROXYACETOPHENONE DERIVATIVES FROM *DORONICUM GRANDIFLORUM*

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In the course of a chemical study of stems and leaves of *Doronicum grandiflorum* Lam. (Compositae) we obtained two known compounds, I and II, which are two *p*-hydroxyacetophenone derivatives previously described in the literature. Compound I was isolated from *Ageratina altissima* and *Trichogonia graziela* (1), and II, from *Trichogonia graziela* only (2). These two compounds belong to the same biosynthetic chain, and II is formed from I. This is the first report of the occurrence of these compounds in the *Senecioneae* Tribe.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded with the following instruments: Ms, AEI, MS 902; ^{1}H nmr, CAMECA 350. Adsorbant for tlc and cc were Kieselgel 60H obtained from Merck and Sephadex LH-20 obtained from Pharmacia.

PLANT MATERIALS.—*D. grandiflorum* was collected in the Alps (France) in July 1982. A voucher is retained in our laboratory (Faculty of Pharmacy, Lyon).

EXTRACTION AND ISOLATION OF THE TWO COMPOUNDS.—Dried and powdered stem and leaf material of *D. grandiflorum* were extracted with $CHCl_3$. The extracts were fractioned on a Sephadex LH-20 column and further purified by silica gel tlc. Two compounds (I and II) were isolated and identified by ms and nmr (before and after acetylation for II). Compound I was: 2-senecioyl-4-(1-hydroxyethyl)-phenol, and compound II was 2,2 dimethyl-6-(1-hydroxyethyl)-chroman-4-one. Our ^{1}H nmr and ms data were in agreement with literature values (1,2).

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

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ISOLATION OF PROVINCIALIN FROM *AGERATINA CRONQUISTII*

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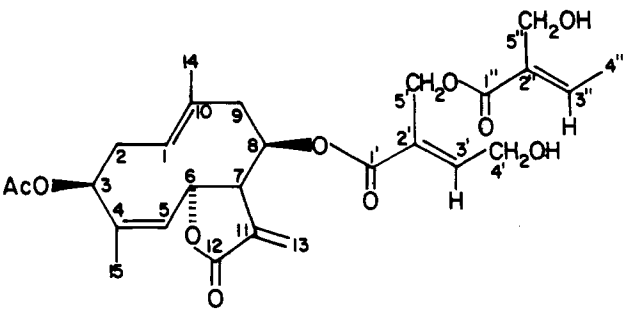
A known sesquiterpene lactone, provincialin (**1**), was isolated as the main constituent of the CH_2Cl_2 extract of the aerial parts of *Ageratina cronquistii* King and Robinson (Eupatorieae, Asteraceae). This compound was previously isolated from *Liatris provincialis* Godfrey, another member of the tribe Eupatorieae



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(1). The identity of our sample was confirmed by comparison of its ^{1}H-nmr, ms, and ir data with those reported in the literature (1,2). In addition, the previously unreported ^{13}C-nmr spectrum gave further support for the structure of provincialin.

EXPERIMENTAL

Aerial parts of *A. cronquistii* (1.27 kg), collected in March, 1982, along Hwy 40, 6.7 mi W of La Ciudad, Durango, Mexico (voucher specimen Gershenzon, McCormick and Warnock No. 301 deposited in the University of Texas Herbarium), were extracted with CH_2Cl_2 and worked up in the usual manner (3). The crude syrup (39 g) was chromatographed over a silica gel column (450 g) packed in CH_2Cl_2 and eluted with a CH_2Cl_2-EtOAc gradient. Fractions of 250 ml each were collected. Provincialin (**1**) (1.5 g) was obtained as a colorless oil from fractions 89-99 (CH_2Cl_2-EtOAc, 20:80) after repeated preparative tlc (2 mm layers of silica gel, CH_2Cl_2-MeOH, 8:1).

PROVINCIALIN (**1**).—Compound **1** is a colorless oil; ms (probe, 70 eV) M^+, 518 (0.7%), fragmentation pattern identical to that reported in the literature (1): ir ($CHCl_3$) max cm^{-1}: 3420, 1761, 1739, 1730, 1652; ^{1}H nmr ($CDCl_3$, 200 MHz) identical to that reported in literature (1); ^{13}C nmr ($CDCl_3$, 22.6 MHz) assignments based upon correlation with provincialin analogs from *Schkuhria virgata* (2): 125.4 (d, C-1), 29.5 (t, C-2), 76.9 (d, C-3), 137.4 (s, C-4), 126.4 (d, C-5), 79.2 (d, C-6), 48.5 (d, C-7), 75.8 (d, C-8), 43.4 (t, C-9), 136.9 (s, C-10), 135.4 (s, C-11), 170.2 (s, C-12), 125.1 (t, C-13), 19.1 (q, C-14), 23.1 (q, C-15), 165.0 (s, C-1′), 126.7 (s, C-2′), 148.3 (d, C-3′), 59.3 (t, C-4′), 58.3 (t, C-5′), 167.3 (s, C-1″), 131.8 (s, C-2″), 142.3 (d, C-3″), 14.3 (q, C-4″), 56.5 (t, C-5″), 170.0 (s, acetate carbonyl), 21.2 (q, acetate methyl).

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MINOR PHENOLIC COMPONENTS OF THE SEEDS OF *GYNANDROPSIS GYNANDRA*

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Kaempferol (1) was previously isolated from the seeds of *Gynandropsis gynandra* (L.) Briquet [syn. *Gynandropsis pentaphylla* DC., *Cleome gynandra* L., and *Cleome pentaphylla* (2)], and the minor components 5,7-dihydroxychromone, 5-hydroxy-3,7,4′-trimethoxyflavone, and luteolin have now been found.

EXPERIMENTAL

PLANT MATERIALS.—The herbaceous plant *G. gynandra* belongs to the family Cleomaceae and is a common weed in the warmer parts of India. The seeds were purchased from the market and identified by Dr. C.R. Babu, Reader, Department of Botany, University of Delhi, Delhi-110 007, India.

EXTRACTION AND ISOLATION OF POLYPHENOLS.—Dried, ground seeds (0.5 kg) were first defatted with petrol (3×1 liter) and then extracted with MeOH (4×1 liter). The methanolic extract was concentrated in vacuo, and the residue (10 g) on column chromatography gave 5,7-dihydroxychromone (3) (200 mg), 5-hydroxy-3,7,4′-trimethoxyflavone (4) (90 mg), and luteolin (5,6) (300 mg).

All the above polyphenols were identified by comparison with authentic samples by ^{1}H nmr, tlc, mp, and mixed mp determinations and by preparation of derivatives. The acetate of 5-hydroxy-3,7,4′-trimethoxyflavone crystallized from EtOH as colorless plates, mp 189-190°; tlc, Rf 0.62 (C_6H_6-EtOAc, 4:5) (Found: C, 64.6; H, 4.8. $C_{20}H_{18}O_7$ requires: C, 64.8; H, 4.9%); ^{1}H nmr 2.42 (s, 3H, OCOCH_3),