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COMPOSITAE

PYROMECONIC ACID IN *PARTHENIUM INTEGRIFOLIUM*

WERNER HERZ and P. S. SLJBRAMANIAM

Department of Chemistry, The Florida State University, Tallahassee, Florida 32306, U.S.A.

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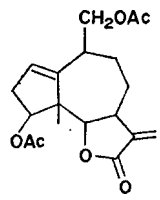
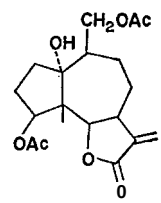
SESQUITERPENE lactone content suggests a relatively close relationship between *Purthenium* (Heliantheae, subtribe Melampodiinae) and *Ambrosia* (Heliantheae, subtribe Ambrosiinae).[1] Since our last survey,[1] a number of additional *Parthenium* species have been studied;[2–6] all *Parthenium* species which were investigated[1,2–6] except *P. argentatum* Gray[7] were found to contain pseudoguaianolides typically with oxygenated methyl groups. Thus, Yoshioka *et al.*[5] isolated tetraneurin C (1) and tetraneurin F (2) from an Illinois collection of *P. integrifolium* L. Prior to the publication of this latter article we had studied a collection of *P. integrifolium* from Pennsylvania. Flowerheads or leaves and stems furnished respectable yields of pyromeconic acid (3-hydroxy-4H-pyran-4-one, 3) previously isolated from *Erigeron annuus*.[8] Sesquiterpene lactones, if present, could not be identified.



1



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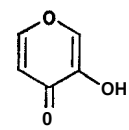

3

EXPERIMENTAL

Extraction of Parthenium integrifolium *L.*

(A) Ground flowerheads wt. 725 g collected by Dr. B. H. Braun on 17 July 1966 near Mill Creek Trail, Virginia, were extracted with $CHCl_3$ and worked up in the usual manner.[9] The crude gum, wt. 6·5 g, was taken up in a small amount of $CHCl_3$ and chromatographed over 200 g of silicic acid (Mallinckrodt 100 mesh) set in benzene, 500 ml fractions being collected. Fractions 1–5 (benzene) and 6-10 (benzene–$CHCl_3$, 3:2) did not elute anything. Fractions 11-16 (benzene–$CHCl_3$, 1: 1) eluted solid material. Recrystallization from Et_2O afforded 1·2 g of pyromeconic acid, m.p. 115-118" (lit.[8] 117–118), NMR signals (DMSO-d_6) 8·0 d and 6·32 d (5.5, AB system, H-5 and H-4), 7.98 (H-2) and 3·3 br (-OH), λ_{max} 214, 272 nm (8300, 7700),

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[2] H. RUESCH and T. J. MABRY, *Tetrahedron* **25**, *805* (1969).
[3] H. YOSHIOKA, H. RUESCH, E. RODRIGUEZ, A. HIGO, J. A. MEARS, T. J. MABRY, J. G. CALZADO and X. A. DOMINGUEZ, *Tetrahedron 26, 2167 (1970).*
[4] A. ROMO DE VNAR, M. AGUILAR, H. YOSHIOKA, A. HIGO, E. RODRIGUEZ, J. A. MEARS and T. J. MABRY, *Tetrahedron 26, 2775* (1970).
[5] H. YOSHIOKA, E. RODRIGUEZ and T. J. MABRY, *J.* Org. *Chem.* 35, 32, 2888 (1970).
[6] A. ROMO DE VNAR, C. GUERRERO and G. WITTGREEN, *Rev. Latinoameric. Quim.* 1, 39 (1970).
[7] L. RODRIGUEZ-HAHN, A. ROMO DE VNAR, A. ORTEGA, M. AGUILAR and J. ROMO, *Tetrahedron 24* (1970). This species contains several triterpenes in addition to the well-known sesquiterpene partheniol.
[8] K. IMAI and S. MAYAMA, *Yakagaku Zasshi 73,128* (1953).
[9] W. HERZ and G. HOGENAUER, *J. Org. Chem. 27, 905* (1962).

in presence of base 262, 318 nm (1900, 5700).[10] (Found: C, 5364; H, 3·67; 0, H, 42.84. Calc, for $C_5H_4O_3$; C, 53.58; H, 3.57; 0, 42.85 %.) Further elution with more polar solvents eluted nothing or small amounts of intractable gums.

(B) Extraction of 1·35 kg of ground stems and leaves collected by Dr. B. H. Braun on 28 August 1966 in the same locality gave 8 g of gum. Chromatography over 180 g of silicic acid gave in fractions 13 and 14 ($CHCl_3$–benzene, 1: 1) a yellow gum showing several spots on the TLC and in fractions 14-21 (benzene–$CHCl_3$, 1: 1) 1·4 g of pyromeconic acid. The more polar fractions eluted nothing or intractable gums.

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[10] K. YAMADA, *Bull. Chem. Soc. Japan 35, 1323* (1962).

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EUPHORBIACEAE

FLAVONOIDS OF THE LEAVES OF *JATROPHA GOSSYPIFOLIA*

S. SANKARA SUBRAMANIAN, S. NAGARAJAN and N. SULOCHANA

Department of Chemistry, Jawaharlal Institute of Postgraduate Medical Education and Research, Pondicherry-6, India

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Plant. Jatropha gossypifolia L.

Occurrence. As a common weed in all plains and waste places.'

Uses. *Medicinal.*[2]

Previous work. Leaves (cyanidin glycoside);[3] on sister species.[4]

Present Work

Leaves. Alcoholic extract of the fresh material fractionated with petrol, ether, ethyl acetate and methyl ethyl ketone. Vitexin (from ethyl acetate fraction, yield, 0·2%, m.p., mixed m.p., not hydrolysable with 25 % MeOH–HCl, hydrolytic fission with HI in phenol, R_f and co-chromatography, UV and IR). Apigenin (from ether fraction, R_f and co-chromatography and acetate). In addition to vitexin, the ethyl acetate and methyl ethyl ketone fractions contained isovitexin (R_f and co-chromatography). The aq. portion, after extraction with methyl ethyl ketone, contained an additional spot with R_f: 0·45 (15% HOAc), 0·71 (30% HOAc), 0.76 (50% HOAc), 0.80 (60% HOAc), 0.65 (BAW 4: 1: 5), 0·81 (Phenol) (Whatman No. 1, temp. 30 ± 2") which gave apigenin with 7% H_2SO_4. Further characterization was not possible due to poor yield.

This is the second instance of occurrence of flavonoid-C-glycoside in Euphorbiaceae, the first one being in ***Croton zambezicus.***[5]

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[1] J. S. GAMBLE, ***Flora of the Presidency of Madras,*** p. 937, Botanical Survey of India, Calcutta (1962).
[2] R. N. CHOPRA, S. L. NAYAR and I. C. CHOPRA, ***Glossary of Indian Medicinal Plants,*** p. 145, Council of Scientific and Industrial Research, New Delhi (1956).
[3] L. PONNIAH and T. R. SESHADRI, ***J. Sci. Ind. Res. India 12B,*** 608 (1953).
[4] ANON, ***Wealth of India, Raw Materials,*** Vol. V, p. 293, C.S.I.R., New Delhi (1959).
[5] H. WAGNER, L. HÖRHAMMER and I. C. KIRLAY, ***Phytochem. 9, 897 (1970).***