Phytochemistry, Vol. 21, No. 12, pp. 2893–2894, 1982.
Printed in Great Britain.

0031-9422/82/122893-02$03.00/0

A 5, 6-DIMETHOXYLATED FLAVONE IN THE LEAF RESIN OF *ADENOSTOMA SPARSIFOLIUM*

MARGARETA PROKSCH, GOTTFRIED WEISSENBOECK* and ELOY RODRIGUEZ

Phytochemical Laboratory, Department of Ecology and Evolutionary Biology, University of California, Irvine, CA 92717, U.S.A.; *Botanical Institute, University of Cologne, Gyrhofstr. 15, 5000 Cologne 41, West Germany

(*Received* 5 *January* 1982)

Key Word Index—*Adenostoma sparsifolium*; Rosaceae; flavonoid; 5,6-dimethoxy-3,7,4'-trihydroxyflavone; leaf resin.

Abstract—A new flavone 5,6-dimethoxy-3,7,4'-trihydroxyflavone was isolated from the external leaf resin of *Adenostoma sparsifolium* and identified by spectroscopic means.

INTRODUCTION

In continuation of our phytochemical analysis of the leaf resin of desert plants, we report the structure elucidation of a new flavonoid 5,6-dimethoxy-3,7,4'-trihydroxyflavone from *Adenostoma sparsifolium* Torr from California and Baja California [1]. The glandular trichomes on the leaf produce a lipophilic resin which coats the leaf surface and exhibits a yellow fluorescence in UV light. Previous investigations of the major flavonoids in the resin of *A. sparsifolium* have established the presence of pinocembrin, galangin, 5,6-dimethoxy-3,7-dihydroxyflavone and 8-methoxy-3,5,7-trihydroxyflavone [2].

RESULTS AND DISCUSSION

The new flavone 5,6-dimethoxy-3,7,4'-trihydroxyflavone (**1**) showed a strong yellow–green fluorescence in UV light. The colour, which did not change after fuming with ammonia, indicated a flavone with a free 3-hydroxyl group and the 5-hydroxyl group either lacking or substituted [3]. The flavone skeleton was substituted by two methoxyl and three hydroxyl groups as indicated by the molecular ion peak at 330 *m/z* [4]. The mass spectrum showing a peak at 121 *m/z* and the observed slight decrease in the sodium methoxide spectrum revealed the presence of a hydroxyl group at the 4' position. This was confirmed by the ^{1}H NMR spectrum with the typical coupling pattern for a 4'-oxygenated B-ring [5]. Location of the remaining two hydroxyl groups at the C-7 and C-3 positions was clear from the different shifts in the UV spectrum; the methoxyl group at the C-5 position was indicated in the ^{1}H NMR by the absence of the deshielded C-5 proton at δ 8 [5]. After permethylation, **1** yielded 3, 5, 6, 7, 4'-pentamethoxyflavone (**2**), the location of the second methoxyl group at C-6 being confirmed by the singlet at δ 6.7 typical for the H-8 proton of a flavone with methoxyl groups at C-5, C-6 and C-7 [6]. The structure of this new flavone is therefore 5,6-dimethoxy-3,7,4'-trihydroxyflavone.

EXPERIMENTAL

The plant material was collected in May 1981 near Oak Grove in San Diego County, California. A voucher specimen is on file in the UCI Herbarium. Extraction and fractionation of the resin was carried out as described before [2]. Fraction 3 contained a mixture of 8-methoxy-3,5,7-trihydroxyflavone and 5,6-dimethoxy-3,7,4'-trihydroxyflavone (**1**). Compound **1** could be isolated by prep. TLC on Cellulose MN 300 in 40% HOAc and purified for further analysis on a Sephadex LH-20 column with MeOH as eluting system. Methylation of **1** was conducted with CH_2N_2 at room temp. for 48 hr yielding 3,5,6,7,4'-pentamethoxyflavone (**2**).

5, 6-*Dimethoxy*-3, 7, 4'-*trihydroxyflavone* (**1**). R_f values on Whatman 3MM: 0.16 (15% HOAc); 0.71 (TBA). UV λ_{max}^{MeOH} nm: 258, 358; NaOMe: 260, 368; $AlCl_3$: 273, 305, 350, 423; $AlCl_3$–HCl: 271, 305, 349, 423; NaOAc: 260, 386; H_3BO_3: 281, 330 sh, 435. ^{1}H NMR (90 MHz, Me_2CO-d_6–TMS, underivatized compound): δ 3.95, 4.0 (6H, 2 *s*, OMe-5, OMe-6); 6.75 (1H, *s*, C-8); 6.9 (2H, *d*, J = 9 Hz, C-3', C-5'); 8.1 (2H, *d*, J = 9 Hz, C-2', C-6'). EIMS (70 eV, probe) *m/z*: 330 $[M]^+$; 315 $[M-OMe]^+$; 287 $[M-MeCO]^+$; 121 $[B_2]^+$ 118 $[B_1]^+$.

3, 5, 6, 7, 4'-*Pentamethoxyflavone* (**2**). ^{1}H NMR (90 MHz, $CDCl_3$, TMS): δ 3.8–4.0 (15H, 5*s*, OMe-3, OMe-5, OMe-6, OMe-7, OMe-4') 6.73 (1H, *s*, C-8); 7.4 (2H, *d*, J = 9 Hz, C-3', C-5'); 8.0 (2H, *d*, J = 9 Hz, C-2', C-6').

Acknowledgements—We thank NSF, NIH (AI 18398) and the UCI Graduate Division (Focused Research Program) for financial support. We also thank Mrs. K. Moore, Department of Chemistry, UCI, for recording the mass spectrum.

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