Isolierung und Identifizierung der Verbindungen Die oberirdischen Teile der Pflanzen wurden zuerst mit MeOH extrahiert Nach Abtrennung des Chlorophylls durch Digerieren des methanolischen Extraktes mit heißem Wasser und Ausschutteln mit $CHCl_3$, Gewinnung eines Flavon-Gemisches durch Extraktion der wasserigen Losung mit Äther und EtOAc, Chromatographie der aus EtOAc erhaltenen Mischkristallisate an Zellulosesaule mit 15%iger Essigsaure bzw Polyamid mit 80%igem MeOH ergab Quercetin, Kampferol und Quercetin-3-*O*-methylather aus *Haplopappus bailahuen*, Quercetin, Kampferol, Myricetin, Myricetin-3-*O*-α-*L*-rhamnosid und Myricetin-3-β-D-galactosid aus *Myrceugenella chequen*; Quercetin, Kampferol und Quercetin-3-*O*-rhamnoglucosid (Rutin) aus *Fabiana imbricata*, und Quercetin-3-rhamnoglucosid (Rutin) aus *Quinchamalium majus*

Die Flavone wurden durch Vergleich mit auth Substanz, Cochromatographie in 3 Systemen, UV- und IR-(bzw NMR) Analyse identifiziert

Es wurden zum ersten Mal Myricetinderivate in Myrtaceae gefunden Ferner wurde der nur noch in Tabakbluten, *Goodenia strophidata*, *Eupatorium* Arten und kürzlich von uns in *Vernonia* Arten[2] gefundene Quercetin-3-*O*-methylather isoliert

Anerkennung—Frau M T Wilkomirsky dankt der Alexander von Humboldt-Stiftung, Bad Godesberg-Bonn, fur die Gewahrung eines Forschungsstipendiums

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Phytochemistry, 1973, Vol 12, pp 2069 to 2071 Pergamon Press Printed in England

ISORHAMNETIN 3-*O*-GLUCOSIDE 7-*O*-ARABINOSIDE FROM *ESCHSCHOLZIA MEXICANA*

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(*Received* 24 *January* 1973 *Accepted* 1 *March* 1973)

Key Word Index—*Eschscholzia mexicana*, Papaveraceae, isorhamnetin 3-*O*-glucoside 7-*O*-arabinoside

In continuation of our phytochemical investigations of medicinal plants from Mexico, we report the isolation and identification of isorhamnetin 3-*O*-glucoside 7-*O*-arabinoside (I) from *Eschscholzia mexicana* Greene

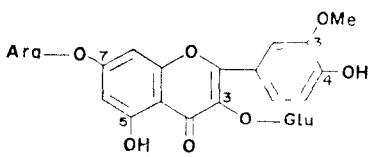
RESULTS AND DISCUSSION

The NMR of the trimethylsilyl ether of I indicated that it was a flavonol with two sugars and one methoxyl group methoxyl signal at 3 96,* aromatic proton signals at 7 8*dd* (*J* 2 5 and 9 0) and 7 41*d* (*J* 2 5) for H-6′ and H-2′, respectively, a doublet at 6 85 (*J* 9 0) for H-5′ and two one-proton doublets at 6 6 and 6 4 (*J* 2 5) for H-8 and H-6 Signals for the anomeric protons of the two sugars were observed at 5 85*c* and 5 0*d* (*J* 6 0) these signals are in agreement with sugars attached at C-3 and C-7 [1]

In benzene-d_6 no significant upfield shift was observed for the signal for the methoxyl group, in accord with the presence of a methylated B-ring in a flavonol 3-*O*-glycoside [2] This observation was confirmed when acid hydrolysis of I yielded isorhamnetin The sugars were identified as arabinose and glucose by paper chromatography and GLC (using their trimethylsilyl ethers) [1,3] The glucosyl moiety must be at C-3 since the NMR signal for the anomeric proton in the trimethylsilyl ether of a flavonol 3-*O*-arabinoside comes around 5 2 while a 3-*O*-glucosyl group always gives a signal near the observed 5 85

Additional information pertaining to the position of attachment of the sugars was obtained by mass spectrometry of the perdeuteriomethylated[4] (PDM) diglycoside (PDM-I refers to I with all hydroxyl groups of the flavonol skeleton and in the sugars deuteriomethylated) That arabinose was at position 7 was indicated when a molecular ion peak for PDM-I was not observed † but a peak at *m/e* 533 appeared instead This ion corresponded to the PDM flavonol arabinoside (that is, minus the glucose moiety) An ion at *m/e* 350 corresponded to isorhamnetin 5,4′-di-deuteriomethyl ether Comparison of PDM-I with the MS of perdeuteriomethylated isorhamnetin 3-*O*-glucoside 7-*O*-rhamnoside showed similar fragmentations, the latter compound exhibited an *m/e* peak at 547 in accord with the loss of the glucosyl group Characteristic fragmentation sugar peaks were observed for both glycosides [4]

Glucosidase hydrolysis of I yielded a compound which appeared yellow when spotted on paper and observed under ultraviolet light, it was identified as isorhamnetin 7-*O*-arabinoside These data together with the spectral findings establish the structure of the flavonol diglycoside as I, to our knowledge, this is the first report of this compound as a natural product



(I)

Note added in proof A substance from *Hunnemannia fumariaefolia*, which was recently forwarded to us [see WAGNER, H, IYENGAR, M A, SELIGMANN, O, BEAL, J L and MITSCHER, L (1973) *Lloydia* in press], was identical with our compound by co-chromatography, MS and UV

* Values are given in ppm (δ-scale) relative to TMS as internal standard *d* = doublet, *dd* = double doublet, *c* = complex

† R D SCHMID[4] observed that of the perdeuteriomethylated flavonoid glycosides recorded, only kaempferol 3,7-dirhamnoside did not exhibit a molecular ion peak (M^+) In our experience, 3-*O*-monosugars in PDM derivatives are often (but not always) cleaved such that an ion containing them is not observed, whereas an ion containing a 7-*O*-monosugar is always observed

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EXPERIMENTAL

Two dimensional chromatograms on Whatman 3MM paper were developed first in TBA (t-BuOH–HOAc–H_2O, 3 1 1), and then in 15% HOAc, NMR spectra of the trimethylsilyl ethers were recorded in CCl_4 and benzene-d_6 using TMS as an internal standard All UV spectra were obtained using standard procedures [1]

Air-dried ground leaf material of *Eschscholzia mexicana* (collected near Monterrey, Mexico*) was extracted with 85% MeOH A yellow amorphorous material (100 mg) precipitated from the extract, the precipitate was purified over polyamide [1] Color test purple (UV) to yellow (UV/NH_3), R_f's TBA 0 27, HOAc 0 71, UV, λ_{max} (nm) MeOH, 355, 270 sh, 257, NaOMe, 402, 270, 250 sh, $AlCl_3$, 400, 368, 300 sh, 270, $AlCl_3$–HCl, 400, 360 sh, 281, NaOAc, 417, 264, NaOAc-H_3BO_3, 360, 270 sh, 258

Mass spectral data for PDM-I *m/e* at 533, 516, 368, 367, 350 (base peak), 322, 321, 230 (PDM-glucose moiety), 196, 184, 183 (PDM-arabinose fragment), 149 and 107 PDM of isorhamnetin 3-*O*-glucoside 7-*O*-rhamnoside 547, 530, 368, 367, 350 (base peak), 321, 230 (PDM-glucose ion), 199, 198, 197 (PDM-rhamnose ion), 145, 127, 121 and 107

Acknowledgements—The work at The University of Texas was supported by the Robert A Welch Foundation (Grant F-130), The National Science Foundation (Grant GB-29576X) and The National Institutes of of Health (Grant HD-04488)

* Voucher XAD-sn is deposited in the Instituto Technologico y de Estudios Superiores de Monterrey Herbarium

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Phytochemistry, 1973, Vol 12, pp 2071 to 2072 Pergamon Press Printed in England

COUMARINS AND ALKALOIDS OF *AEGLE MARMELOS**

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(*Received* 20 *March* 1973 *Accepted* 6 *April* 1973)

Key Word Index—*Aegle marmelos*, Rutaceae, psoralen, xanthotoxin, *o*-methylscopoletin, scopoletin, tembamide, skimmin

The ubiquitous usage[1 2] of *Aegle marmelos* Corr in the indigenous system of Indian medicine and the observed hypoglycaemic activity of the crude alcoholic extract of its root in rats prompted us to undertake the present investigation A number of alkaloids,[3–7] coumarins,[5,7–9] sterols[6,8,9] and essential oils[10] have previously been isolated from this plant

The EtOAc soluble fraction of the alcoholic extractive of the root on column chromatography over silica gel afforded the constituents outlined below

Psoralen, 37 mg ($C_{11}H_6O_3$), m p and m m p 169–170°, eluted with C_6H_6 UV λ_{max}^{EtOH} 240

* Communication No 1836 from Central Drug Research Institute, Lucknow

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