1208. PMR [$(CD_3)_2CO$, τ]: −3·30 (*s*, O<u>H</u>-5), 1·84 (*s*, H-2), 2·74 (*d*, *J* 2 Hz, H-2'), 2·90 (*dd*, *J* 8 and 2 Hz, H-6'), 3·14 (*d*, *J* 2 Hz, H-5'), 3·57 (*d*, *J* 2 Hz, H-8), 3·70 (*J* 2 Hz, H-6), 6·10 (*s*, OC<u>H</u>$_3$). MS: M + 1 301 (16%), M 300 (100%), *m/e* (%) 299 (9), 285 (11), 284 (12), 271 (10), 268 (36), 257 (11), 229 (15), 179 (9), 177 (9), 163 (10), 153 (34), 149 (16), 148 (16), 137 (10), 135 (11), 134 (15), 133 (23), 132 (38), 124 (10), 123 (9), 120 (15), 117 (13), 105 (23). *Triacetate*, m.p. 184–186° (C_6H_6). λ_{min}^{KBr} (cm^{-1}): 1745, 1617, 1505, 1430, 1365, 1270, 1200, 1125, 1030, 910. PMR [$(CD_3)_2CO$, τ]: 1·58 (*s*, H-2), 2·53 (*d*, *J* 2 Hz, H-8), 2·72 (sec. split *d*, H 9 Hz, H-5', H-6'), 2·78 (*d*, superimp. on part of preceding, H-2'), 2·91 (*d*, *J* 2 Hz, H-6), 6·10 (*s*, OC<u>H</u>$_3$), 7·62 (*s*, two COC<u>H</u>$_3$), 7·70 (*s*, COC<u>H</u>$_3$).

Phytochemistry, 1974, Vol. 13, pp. 752 to 753. Pergamon Press. Printed in England.

AZAFRIN FROM ROOTS OF *PEDILANTHUS TITHYMALOIDES*

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(*Received* 29 *September* 1973. *Accepted* 27 *October* 1973)

Key Word Index—*Pedilanthus tithymaloides*, Euphorbiaceae, azafrin.

Plant. Pedilanthus tithymaloides, dried Roots. *Source.* Supplied by Dr. Steinmetz, Amsterdam, The Netherlands. *Previous work.* Epifriedelanol acetate, friedelin, epifriedelinol, 1-dotriacontanol and β-sitosterol.[1]

Dried roots. Within a programme to study the occurrence and distribution of irritants and cocarcinogens in plants 1 kg of roots were Soxhleted with diverse solvents of increasing polarity as follows, and the irritation units (IU) and irritation doses 50 (ID_{50}) on the mouse ear determined following the standard procedure:[2] EtOAc (35·1 g, IU: 1500 μg/ear, ID_{50}: 150 μg/ear), Et_2O (26 g, IU: >848 μg/ear, ID_{50}: 213 μg/ear), $CHCl_3$ (9·2 g, IU: >630 μg/ear) and *n*-PrOH (3·5 g, IU: >650 μg/ear). After treatment with perchloric acid in MeOH no increase in the irritation activity was observed in any extract. The ETOAc extract on silica gel column, deactivated with 13% H_2O, upon elution with Et_2O-light petrol, (1:1), gave a compound with MS and R_f value identical with that of azafrin.[4] MW: *m/e*, 426 (22·6%), 408 (7·6%), 393 (1·9%), 382 (3·8%), 375 (1·9%), 364 (1·89%), 349 (1·88%), 347 (1·9%), 328 (5·7%), 327 (15·4%), 316 (1·9%), 299 (1·9%), 133 (13%), 109 (100%), 91 (21·3%), 83 (5·45%), 73 (1·9%), 69 (39·2%), 59 (4·7%), 43 (53·5%). R_f = 0·05 (Et_2O-petrol., on Merck silica gel $60F_{254}$, TLC, pre-coated plate). It appears from this observation that the dried roots do not contain irritant principles such as 12,13-di- or 13-monoesters of phorbol and

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related diterpenes derivatives,[3,5] or cryptic irritants such as 12,13,20-tri-esters of phorbol and related diterpenes.[3,5]

Acknowledgements—The authors are thankful to Professor S. L. Jensen, Norwegian Institute of Technology, Trondheim, Norway, for the authentic sample of azafrin. R. R. Upadhyay is grateful to the Alexander von Humboldt Foundation Bad Godesberg, Germany, for a Research fellowship.

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Phytochemistry, 1974, Vol. 13, p. 753. Pergamon Press. Printed in England.

FLAVONES AND FLAVONOLS IN EXUDATE OF *SALVIA GLUTINOSA*

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(*Received* 24 *September* 1973. *Accepted* 16 *October* 1973)

Key Word Index—*Salvia glutinosa*; Labiatae; flavonoids; kumatakenin; ayanin; retusin.

Plant. Salvia glutinosa L. *Source.* Botanical Garden, University of Heidelberg. *Previous work.* α-Amyrin, ursolic acid and nonacosane from flowers and calyces of *S. glutinosa*;[1] sterols and flavone salvigenin from *S. triloba*;[2] ultrastructure of glands of *S. glutinosa*.[3]

Present work. Aereal parts of whole plant were dipped into Et_2O and the solution concentrated to give an oil.* Separation into several fractions was effected on a column of silica gel (C_6H_6/increasing quantities of MeCOEt and MeOH) to give α-amyrin as the main component, other lipid material (not identified, comp.[1]) and flavonoids. Isolation of pure flavonoids was by preparative TLC on polyamide (C_6H_6–petrol.–MeCOEt–MeOH, 60:26:7:7 and C_6H_6–dioxane–MeOH, 8:1:1[4]) and identification by co-chromatography with authentic samples and UV spectra.

RESULTS

The lipophilic exudate of *Salvia glutinosa* contains very small amounts of the flavones apigenin and gengkwanin (apigenin 7-methyl ether), and of the flavonols isokaempferide (kaempferol 3-methyl ether), kumatakenin kaempferol 3,7-dimethyl ether; UV λ_{max} 350 and 268 nm, with added $AlCl_3$ shift to 394 nm, with added NaOEt shift to 390 nm, no shift with NaOAc), ayanin (quercetin 3,7,4′-trimethyl ether; UV λ_{max} 355 and 256 nm, with added $AlCl_3$ shift to 398 nm, with added NaOEt shift to 398 nm, no shift with NaOAc), and possibly retusin (quercetin 3,7,3′,4′-tetramethyl ether; concluded from TLC comparison only).

* *Acknowledgement*—Thanks are due to Professor E. Schnepf and Miss G. Deichgräber from Heidelberg University for supplying this extract.

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