

—117.5°; (α)₃₁₆ —191.5°. IR, $\bar{\nu}$ 3450, 2900, 1620, 1450, 1362, 1075, 1064, 1042, 1020, 998, 917, 833 cm^{-1} . NMR, δ 6.3–5.8 (1H, *dd*), 5.3–4.8 (2H, *m*), 3.8–3.3 (2H, *dd*), 1.25 (3H, *s*), 1.15 (3H, *s*), 0.9 (3H, *s*), 0.85 (3H, *s*).

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REFERENCES

1. Hegnauer, R. (1973) *Chemotaxonomie der Pflanzen*, Birkhauser Verlag.
2. Domínguez, X. A. (1973) *Métodos de Investigación Fitoquímica*, Limusa Wiley, Mexico.

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α - AND β -AMYRIN ESTERS AND SITOSTEROL GLUCOSIDE FROM *SPILANTHES ACMELLA*

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Key Word Index—*Spilanthes acmella*; Compositae; fatty acid esters of α - and β -amyrins; myricyl alcohol; stigmasterol; sitosterol-*O*- β -D-glucoside.

Plant. *Spilanthes acmella* Linn. (Voucher specimen No. C-1/73, deposited at the Department of Botany, Bangalore University.) **Uses.** Medicinal [1, 2]. **Previous work.** Spilanthol [3–5]; on sister species [6–8]. **Present work.** Air-dried whole plant of *S. acmella* was extracted with light petrol, followed by 90% EtOH. The light petrol extract when subjected to adsorption chromatography over neutral Al_2O_3 yielded the following fractions: (a) A viscous semi-solid (light petrol eluate), homogeneous on TLC; IR spectrum showed ester CO. Hydrolysis with methanolic alkali yielded a mixture of α - and β -amyrins, separated and identified as their acetates. Methanolysis of the parent ester with methanolic HCl followed by GLC, showed lauric, myristic, palmitic (major component), linoleic and linolenic acids as their methyl esters. (b) Mixture of α - and β -amyrin acetates (light petrol- C_6H_6 , 4:1), separated by repeated fractional crystallization from

MeOH and subsequently from CHCl_3 - Et_2O ; identities confirmed by direct comparison with authentic samples (mp, mmp, $[\alpha]_D$ and IR.) (c) Myricyl alcohol (light petrol- C_6H_6 , 2:1 eluates), mp 85–86°, acetyl derivative, mp 71–72° on direct comparison with authentic samples. (d) Mixture of α - and β -amyrins (light petrol- C_6H_6 , 1:1 eluates) separated and identified through their acetates and (e) Stigmasterol (light petrol- C_6H_6 , 1:2 eluates), mp, mmp, acetyl, co-TLC.

The ether extract of the alcoholic concentrate gave an amorphous green solid which was purified by adsorption chromatography over Si gel (CHCl_3 -MeOH, 92:8 eluates) and subsequent crystallization from dioxan to yield sitosterol-*O*- β -D-glucoside, mp 304–306°; tetra acetate, mp 168–170°, $[\alpha]_D^{25}$ —31.6° (CHCl_3). It was hydrolysed to sitosterol and D-glucose. The identities of the glucoside and its acetate were confirmed by direct comparison with authentic samples (mp, co-TLC, NMR [9], IR).

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The absence of any sesquiterpene lactone in *S. acmella* is quite significant.

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REFERENCES

1. Watt, J. M. and Breyer-Brandwijk, W. G. (1962) *The Medicinal and Poisonous Plants of Southern and Eastern Africa*, p. 292. E & S Livingstone, London.
2. Chopra, R. N., Nayar, S. L. and Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants*, p. 232. C.S.I.R., New Delhi.
3. Pendse, G. S., Phalnikar, N. L. and Bhide, B. V. (1945) *Current Sci.* **14**, 37.
4. Gokhale, V. G. and Bhide, B. V. (1945) *J. Ind. Chem. Soc.* **22**, 250.
5. Crombie, L., Krasinski, A. H. A. and Manzoor-I-Khuda (1963) *J. Chem. Soc.* 4970.
6. Gerber, E. (1903) *Arch. Pharm.* **236**, 270.
7. Asano, M. and Kanematsu, T. (1932) *Chem. Ber.* **65B**, 1602.
8. Jacobson, M. (1957) *Chem. Ind.* 50.
9. Sucrow, W. (1966) *Chem. Ber.* **99**, 2765.

Phytochemistry, 1975, Vol. 14, pp. 1667–1668. Pergamon Press. Printed in England.

2-HYDROXYPHENYL ACETIC ACID AND 2,4-DIHYDROXYPHENYL ACETONITRILE FROM *ERICA SCOPARIA*

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Key Word Index—*Erica scoparia*; Ericaceae; (2-hydroxyphenyl) acetic acid; (2,4-dihydroxyphenyl) acetonitrile.

Several phenolic compounds have been identified in the Ericaceae [1] but *E. scoparia* has not so far been investigated. On paper chromatograms of leaf extracts of this plant, we observed a large, red-purple, uncommon spot after spraying with diazotized *p*-nitroaniline. The compound causing this reaction was present in the NaHCO₃ soluble part of the extractives. After isolation it was identified as 2-hydroxyphenyl acetic acid. Previously, this compound has been found only twice in higher plants, namely in *Astilbe* (Saxifragaceae) [2] and in *Miscanthus floridulus* (Labill.) Warb [3]. The compound has also been found in *Penicillium* cultures [4,5]. Both the biosynthesis and metabolism of hydroxyphenyl acetic acids in higher plants have been studied [6].

From the fraction of the extract not soluble in NaHCO₃ we isolated a substance with chromatographic behaviour similar to orcinol. NMR and mass spectral analysis, however, showed this compound to be a dihydroxyphenyl acetonitrile. The chemical shifts and the coupling constants

of the aromatic protons pointed to the hitherto unknown 2,4-dihydroxyphenyl acetonitrile. This was confirmed by synthesis. Firstly the known 3,4-dihydroxyphenyl acetonitrile [7] was prepared for comparison. An attempt to synthesize 2,4-dihydroxyphenyl acetonitrile similarly by demethylation of 2,4-dimethoxyphenyl acetonitrile [8] failed. The compound was finally prepared, albeit in very low yield, in an analogous way to the known synthesis of 2-hydroxyphenyl acetonitrile [9].

Whether or not 2,4-dihydroxyphenyl acetonitrile in *E. scoparia* is formed enzymatically during the extraction procedure from the corresponding glucosinolate, which seems to be the case with other nitriles found in plants [10], is still an open question. Nevertheless, both 2-hydroxyphenyl acetic acid and the novel 2,4-dihydroxyphenyl acetonitrile may be interesting compounds in the taxonomic classification of the Ericaceae.

EXPERIMENTAL

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Material. Leaves of *Erica scoparia* (L.) were collected in July 1973 in Leboreiro, La Coruña (Spain). A sample of the whole