

FLAVONOIDS OF *ORYCTES* (SOLANACEAE)

JOHN E. AVERETT and WILLIAM G. D'ARCY

Department of Biology, University of Missouri—St Louis, St Louis, MO, 63121, U.S.A. and Missouri Botanical Garden, P.O. Box 299, St Louis, MO, 63166, U.S.A.

(Received 21 March 1983)

Key Word Index—*Oryctes nevadensis*; Solanaceae; flavonoid; flavonol; quercetin; chemosystematics.

Abstract—*Oryctes* is a rare monotypic genus of the Solanaceae. It is endemic to the western United States in Inyo County California and adjacent Nevada. Two flavonols, quercetin 3-*O*-rutinoside and quercetin 3-*O*-rutinoside-7-*O*-glucoside were found to be present in methanolic leaf extracts of each of the three populations of *O. nevadensis* sampled.

INTRODUCTION

Oryctes is a rare monotypic genus of the western United States known from Inyo County, California and adjacent Churchill, Esmeralda and Washoe Counties of Nevada. Rydberg [1], in his treatment of *Physalis* and related genera, included *Oryctes* and noted similarities between the genus and *Chamaesaracha*. In particular, he pointed out features of the fruiting calyx and overall habit of *Oryctes* and *Chamaesaracha*. Although these similarities exist, *Oryctes* is easily distinguished by its flower and fruit characters, and its relationship to any of the physaloid genera is obscure [2]. As a part of our overall interest in the Solanaceae, we are reporting the flavonoids for *Oryctes*. This represents the first report of flavonoids from this genus.

RESULTS

Methanolic leaf extracts of *Oryctes nevadensis* Wats yielded two flavonols: quercetin 3-*O*-rutinoside and quercetin 3-*O*-rutinoside-7-*O*-glucoside. The two compounds were present in readily detectable concentrations and heavier applications of extract gave no indication of the presence of additional compounds. Both compounds were present in each of the populations sampled.

DISCUSSION

Oryctes was treated by Bentham and Hooker [3] as a member of tribe Solaneae and placed between *Discopodium* of Central Africa and *Margaranthus* of the southwestern United States and Mexico. Wettstein [4] divided the Solance into five subtribes, placing *Oryctes* as a member of the subtribe Lyciinae along with *Discopodium*, *Margaranthus* and thirteen other genera, mostly of tropical American distribution. *Lycium*, which gives the subtribe its name, also has species in the southwestern United States. Rydberg, however, placed *Oryctes* in the subtribe Solaninae which includes *Solanum*, *Chamaesaracha*, *Brachistus* and other genera. The flavo-

noids present in *Oryctes* are common to much of the Solanaceae including *Leucophysalis* and *Chamaesaracha*, members of tribe Solaneae [5–7]. Unfortunately, few (or none) of the genera of the Lyciinae or those grouped around *Oryctes* by Bentham and Hooker have been analysed for flavonoids. The taxonomic utility of the flavonoids in *Oryctes* is, at this point, uncertain. There is, on the basis of flavonoids, no reason to exclude *Oryctes* from either the Lyciinae or Solaninae, and as a consequence, conclusions must await analysis of additional genera in this diverse and interesting family.

EXPERIMENTAL

Leaves were obtained from three populations of *Oryctes nevadensis*. Voucher specimens are as follows: Nevada, Esmeralda County, Belleville. In open sand, 1700 m., Shockley 272 (UC); Nevada, Washoe County, sandy foothills, Wadsworth, Kennedy 2034 (MO); California, Inyo County, in fine alkaline sand, 4 mi S of Aberdeen (Owens County), Kerr 473 (US).

The material was ground and extracted overnight in 85% MeOH. The quantity of leaf material was ca 0.5 g for each of the populations. Sufficient MeOH was added to just cover the ground leaf material. The resulting extract was examined by 2D-PC and 1D-TLC (polyamide). For structural elucidation, replicate paper chromatograms were run and the isolated compounds were cut from the paper for further purification and analysis. Identification of the glycosides and their aglycones was accomplished by standard spectroscopic, co-chromatographic and hydrolytic techniques [8–11].

Acknowledgements—Individual research grants from the U.S. National Science Foundation to J.E.A. and W.G.D. are gratefully acknowledged.

REFERENCES

1. Rydberg, P. A. (1896) *Mem. Torrey Bot. Club* 4, 297.
2. Averett, J. E. (1979) in *The Biology and Taxonomy of the Solanaceae* (Hawkes, J. G., Lester, R. N. and Skelding, A. D.,

- eds). Academic Press, London.
3. Benthams, G. and Hooker, J. D. (1876) *Solanaceae in Genera Plantarum* Vol. 2, Part 1, p. 882.
 4. Wettstein, R. von (1895) in *Natürlichen Pflanzenfamilien* (Engler, A. and Prantl, K., eds), Vol. IV, Part 3b, p. 3. Wilhelm Engelmann, Leipzig.
 5. Averett, J. E. and Mabry, T. J. (1971) *Phytochemistry* **10**, 2199.
 6. Averett, J. E. (1973) *Rhodora* **75**, 325.
 7. Averett, J. E. and Judd, J. W. (1977) *Biochem. Syst. Ecol.* **5**, 279.
 8. Mabry, T. J., Markham, K. R. and Thomas M. B. (1970) *The Systematic Identification of Flavonoids*. Springer, Berlin.
 9. Averett, J. E. (1977) *Phytochem. Bull.* **10**, 10.
 10. Hiermann, A., Exner, J., Becker, H. and Averett, J. E. (1978) *Phytochem. Bull.* **11**, 55.
 11. Exner, J., Averett, J. and Becker, H. (1977) *Phytochem. Bull.* **10**, 36.

Phytochemistry, Vol. 22, No. 10, pp. 2326–2327, 1983.
Printed in Great Britain.

0031-9422/83 \$3.00 + 0.00
© 1983 Pergamon Press Ltd.

ISOFLAVONOIDS FROM THE HEARTWOOD OF *PTEROCARPUS MARSUPIUM*

J. MITRA and T. JOSHI

Department of Chemistry, University of Allahabad, Allahabad, India

(Revised received 24 March 1983)

Key Word Index—*Pterocarpus marsupium*; Leguminosae; retusin 7-glucoside; irisolidone 7-rhamnoside; 5,7-dihydroxy-6-methoxyisoflavone 7-rhamnoside.

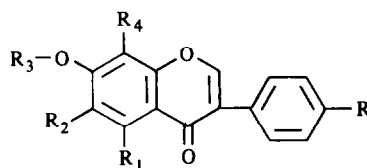
Abstract—Three new isoflavone glycosides viz retusin 7-glucoside, irisolidone 7-rhamnoside and 5,7-dihydroxy-6-methoxyisoflavone 7-rhamnoside have been isolated from the heartwood of *Pterocarpus marsupium*.

Species of *Pterocarpus* are known to be rich in isoflavonoids and terpenoids [1]. From the ethanolic extract of the heartwood of *P. marsupium* three new isoflavone glycosides (1–3) and the known compound 7-hydroxy-5,4'-dimethoxy-8-methylisoflavone 7-rhamnoside [2] were identified.

Compound 1 was found to be glycosidic in nature and on hydrolysis it gave D-glucose (co-PC and osazone) and retusin [3] (7,8-dihydroxy-4'-methoxyisoflavone), which was identified from its colour reactions, UV and ¹H NMR spectral data, alkali fission and ¹H NMR of its acetate. The sugar moiety was found to be attached at the 7-position by comparison of the spectral shifts of the aglycone and glycoside, the glycoside giving no bathochromic shifts of band II with aluminium chloride, aluminium chloride–hydrochloric acid, sodium acetate or sodium acetate–boric acid. This was confirmed by acid hydrolysis of the methylated glycoside to give 8-O-methylretusin [3]. Periodate oxidation confirmed that the glucose was in the pyranose form since it consumed 2 mols of periodate per mol of the glycoside and liberated 1 mol of formic acid. The glycoside was hydrolysed by almond emulsin indicating a β-linkage. Thus, the structure of 1 was confirmed as retusin 7-O-β-D-glucopyranoside. This is the first report of 1 in nature.

Compound 2 was also found to be glycosidic in nature

and acid hydrolysis gave an aglycone and L-rhamnose (co-PC and osazone). The aglycone was characterized as 5,7-dihydroxy-6,4'-dimethoxyisoflavone (irisolidone) [4] from its UV and ¹H NMR spectra and alkali fission to give iretol [5] and p-methoxyphenylacetic acid. Glycosidation was confirmed at position 7 by comparison of the UV spectral shifts and colour reactions of the aglycone with those of the glycoside. The glycoside gave no shift with sodium acetate but gave 13 and 12 nm bathochromic shifts (band II) with aluminium chloride and aluminium chloride–hydrochloric acid reagents, respectively showing the presence of a free hydroxyl at C-5. The structure of 2 was further confirmed by acid hydroly-



- 1 R₁ and R₂ = H, R₃ = Glc, R₄ = OH, R' = OMe
- 2 R₄ = H, R₁ = OH, R₂ and R' = OMe, R₃ = Rha
- 3 R₄ = H, R₁ = OH, R₃ = Rha, R₂ = OMe, R' = H