

officinalis: loganin and morroniside,² morroniside (in fruits)³ *Present work* Acetylation of an iridoid glycoside fraction (700 mg), obtained by the method previously described⁴ from frozen leaves (300 g, collected in September, processed in December, 1971) of *C officinalis*, followed by preparative TLC separation (silica gel-Et₂O-C₆H₆) of the reaction mixture, yielded, as the major product, the tetraacetate of loniceriside⁵ (secologanin⁶), a glucoside previously encountered in leaves of *Lonicera morrowii* A Gray (Caprifoliaceae)⁵ The non-crystalline tetraacetate, exhibiting the expected and almost completely interpreted NMR spectrum, crystallized on seeding with an authentic specimen of loniceriside tetraacetate, kindly provided by Professor Mitsuhashi, Hokkaido University, Sapporo, Japan The purified product melted at 111–112°, alone or in admixture with the authentic specimen (reported⁵ m p 115–116°) Similar processing of leaves of *C mas* gave identical results

Feeding experiments previously established that loniceriside is a precursor for morroniside in fruits of *C officinalis*³ The present finding ascertains that loniceriside is, in fact, a true intermediate on the pathway from loganin to morroniside

Acknowledgement—The authors are grateful to Dr E Hartmann, The Arboretum, Hørsholm, Denmark for providing and identifying the plant material employed in the present study

² ENDO, T and TAGUCHI, H (1970) *Lecture*, quoted after Ref 3

³ INOUE, H, UEDA, S and TAKEDA, Y (1971) *Tetrahedron Letters* 4069

⁴ ROSENDAL JENSEN, S, KJÆR, A and JUHL NIELSEN, B (1973) *Acta Chem Scand* 27, in press

⁵ SOUZU, I and MITSUHASHI, H (1970) *Tetrahedron Letters* 191

⁶ BATTERSBY, A R, BURNETT, A R and PARSONS, P G (1968) *Chem Commun* 1280

Phytochemistry, 1973, Vol 12, pp 2065 to 2066 Pergamon Press Printed in England

GENIPOSIDE AND MONOTROPEIN IN *CORNUS SUECICA*

S ROSENDAL JENSEN, ANDERS KJÆR and B JUHL NIELSEN

Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

(Received 31 March 1973 Accepted 1 May 1973)

Key Word Index—*Cornus suecica*, Cornaceae, geniposide, monotropein, iridoid glucosides

Plant *Cornus suecica* L (subgenus *Arctocrania* Endl)¹ *Source* Rold Skov, Denmark *Previous work* Aucubin, weak reaction on paper chromatography² *Present work*. Whole frozen plants (385 g) were extracted with 75% EtOH The water-soluble part was extracted with BuOH (4 × 30 ml) and divided into a soluble fraction, A (4.1 g), and a residue, B (14.0 g) After treatment with Al₂O₃,³ A gave 0.38 g of mixture, purified by preparative TLC (CHCl₃-MeOH, 3:1) Two recrystallizations from wet EtOAc of the major fraction (144 mg) afforded pure geniposide (46 mg), m p 161–162°, [α]_D²³ +8.7° (c 2.2, H₂O) [lit values⁴ m p 163–164°, [α]_D +7.5°, H₂O], identified by its characteristic ¹H NMR

¹ WANGERIN, W (1910) in *Das Pflanzenreich* (ENGLER, A, ed), Vol IV, p 1, Engelmann, Leipzig

² WINDE, E (1959) *Untersuchungen über die Verbreitung der Pseudoindikane*, Dissert Dahlem/Berlin

³ STICHER, O (1969) *Pharm Acta Helv* 44, 453

⁴ INOUE, H, SAITO, S, TAGUCHI, H and ENDO, T (1969) *Tetrahedron Letters* 2347

spectrum (D₂O, δ -values, extern standard TMS) 7.80 (*d*, *J* 1.0 Hz, H-3), 6.12 (*m*, H-7), 5.51 (*d*, *J* 7.0 Hz, H-1), 5.18 (*d*, *J* 8.0 Hz, anom H), 4.53 (*br s*, 2H, H-10), and 4.00 ppm (*s*, 3H, OCH₃) *Penta-acetate* (Ac₂O in pyridine), m.p. 133–133.5°, [α]_D²¹ + 6.2° (*c* 2, MeOH) [lit. values ⁴ m.p. 133.5–134°, [α]_D + 16.6° MeOH] ¹H NMR data (CDCl₃, δ -values) 7.45 (*d*, *J* 1.0 Hz, H-3), 5.85 (*m*, H-7), 4.75 (*br s*, 2H, H-10), 3.75 (*s*, 3H, OCH₃), 3.16 (*m*, H-5), and 2.0–2.15 ppm (15H, OAc)

On repeated chromatography on columns of silica gel [solvents, BuOH–MeOH–H₂O, 7:1:3, and EtOAc–PrOH–H₂O, 5:3:2] fraction *B* yielded, apart from geniposide (230 mg), another component (blue with SbCl₃) which, after acetylation and preparative TLC (Bz–EtOAc–MeOH, 3:1:1), afforded monotropein penta-acetate (32 mg), m.p. 168–170°, [α]_D²¹ –92° (*c* 0.8, EtOH) [lit. values m.p. 173–174.5°, ⁵ 165.9–167.7° [α]_D¹⁸ –82.5° (*c* 0.8, EtOH), ⁵ [α]_D²³ –94.25° (*c* 1.08, EtOH)⁶], exhibiting an ¹H NMR spectrum identical with that recorded ⁶

Though new to Cornaceae, monotropein has been previously encountered in a number of families, geniposide solely within Rubiaceae. Their joint appearance in *Cornus suecica*, however, seems unprecedented.

Acknowledgements—The authors are grateful to Mr O. Host, the Department of Botany of the Royal Veterinary and Agricultural College, Copenhagen, for kindly providing some of the plant material used in the present study.

⁴ INOUE, H., ARAI, T. and MIYOSHI, Y. (1964) *Chem Pharm Bull* **12**, 888

⁵ STICHER, O. (1971) *Pharm Acta Helv* **46**, 121

Phytochemistry, 1973, Vol. 12, pp. 2066 to 2067 Pergamon Press Printed in England

NAPHTHAQUINONES FROM *DIOSPYROS* AND *EUCLEA* SPECIES

JAMES TANNOCK*

Department of Chemistry, University of Rhodesia, P.O. Box MP 167, Salisbury, Rhodesia

(Received 2 March 1973 Accepted 16 March 1973)

Key Word Index—*Diospyros*, *Euclea*, Ebenaceae, naphthaquinones, euclein, isodiospyrin, 7-methyljuglone

Nineteen species of the Ebenaceae are known to occur in Rhodesia,¹ some of which have previously been examined, and the presence of naphthaldehydes,² and mono- and binaphthaquinones^{3,5} reported. Our interest in chemical plant taxonomy has led to a study of the hexane extracts of the stems of a further seven locally occurring species.

* Present address: Department of Chemistry and Soil Science, P.O. Box 8100, Caueeway, Salisbury, Rhodesia

¹ ANON (1893/1966) *Index Kewensis*, Oxford University Press, Oxford, WHITE, F., personal communication

² HARPER, S. H., KEMP, A. D. and TANNOCK, J. (1970) *J Chem Soc C*, 626

³ FERREIRA, M. A., COSTA, A. C. and ALVES, CORREIA, A. (1972) *Plant Med Phytother* **6**, 32

⁴ VAN DER VIJVER, L. M. and GERRITSMAN, K. W. (1973) *Phytochemistry* **12**, 230

⁵ TEZUKA, M., TAKAHASHI, C., KUROYANAGI, M., SATAKE, M., YOSHIHARA, K. and NATORI, S. (1973), *Phytochemistry* **12**, 175, and references therein