

FLAVONOIDS FROM THE SEEDS OF SIX *Lonchocarpus* SPECIES

F. DELLE MONACHE, L. E. CUCA SUAREZ and G. B. MARINI-BETTOLO

Centro Chimica dei Recettori del C.N.R., Università Cattolica del S. Cuore, Via della Pineta Sacchetti, 644, 00168 Roma, Italy

(Received 6 March 1978)

Key Word Index—*Lonchocarpus*; Leguminosae; flavonoids; rotenoids; 3-hydroxyisolonchocarpin.

INTRODUCTION

In connection with the International Conference on Leguminosae to be held in London in 1978, we have begun a systematic investigation of flavonoids and rotenoids in the Leguminosae with a special emphasis on the two closely related genera, *Lonchocarpus* and *Derris*. A wide range of flavonoids and rotenoids have previously been reported in *L. longistylus* [1], *L. neuroscapha* [2], *L. laxiflorus* [3], *L. utilis* [4], *L.* (or *D.*) *urucu* [5, 6], *L.* (or *D.*) *obtusa* [7], *D. amazonica* [5], *L. floribundus* [5], *D. sericea* [8], *D. chinensis* [4], *D. elliptica* [6], *D. malaccensis* [9], *L. rariflorus* [10], *D. robusta* [11], *D. scandens* [12], and *D. glabrescens* [13].

In this paper we report the results obtained for six further species of *Lonchocarpus*: *L. peninsularis*, *L. xuul*, *L. eriocaulinalis*, *L. unifolius*, *L. sericeus* and *L. capassa*.

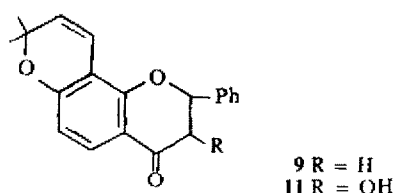
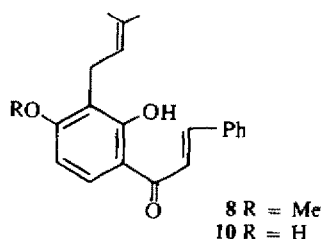
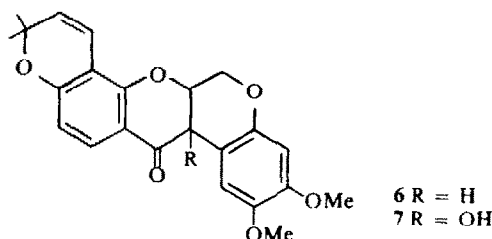
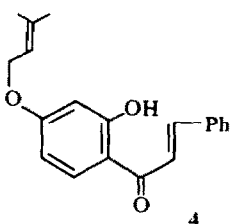
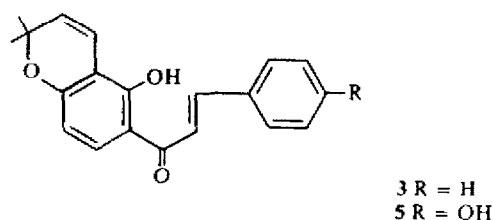
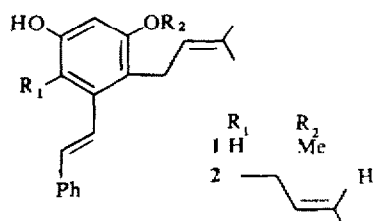
RESULTS

Compounds were identified in the conventional way by direct comparison (mmp, TLC and NMR) with authentic samples previously isolated in our laboratory.

From *L. peninsularis* two prenylated stilbenes, longistylane C, 1 and longistylane D, 2, whose structures were recently elucidated by us [1], were isolated. From *L. xuul* three chalkones were identified: lonchocarpin, 3, derricidin (cordoin), 4 and 4-hydroxylonchocarpin, 5. In *L. unifolius* two rotenoids, deguelin, 6 and tephrosin, 7 were present. Three samples of *L. capassa* from different sources were examined, but no flavonoids or rotenoids were detected.

From *L. sericeus* the following compounds were identified: lonchocarpin, 3, derricin, 8, derricidin (cordoin), 4, isolonchocarpin, 9, isocordoin 10 and 4-hydroxylonchocarpin, 5. Root bark of this species from NE of Brazil has previously been shown [8] to contain all but two of these compounds. The apparent absence of isocordoin and 4-hydroxylonchocarpin from the Brazilian sample is probably due however to the use of hexane rather than methanol for extraction.

From *L. eriocaulinalis* two compounds were isolated. Isolonchocarpin, 9, was the main component; the minor one proved to be a new flavonol. On the basis of analytical data and of the molecular peak (M^+ 322) in the mass spectrum, a molecular formula $C_{20}H_{18}O_4$ was deduced.



UV spectrum suggested a flavanone or 3-hydroxy-flavanone structure without a hydroxyl in the 5 position. From these data and from the NMR spectrum (see Experimental) the structure, 11, 3-hydroxyisolonchocarpin, was assigned to the new compound. The structure was confirmed by Algar-Flynn synthesis from *O*-benzyl-lonchocarpin according to the method of Chopin *et al.* [14].

From these and previously reported results [1-13], it may be deduced that prenylated flavonoids are almost ubiquitous in *Lonchocarpus* and *Derris* species, whereas rotenoids are limited only to some species (*L. unifolius*, *D. malacensis* [9], *D. elliptica* [6], *D. chinensis* [4], *L. utilis* [4], and *L. or D. urucu* [5, 6]). Prenylated flavonoids may be considered biogenetic precursors of the rotenoids. Rarer components are prenylated stilbenes (*L. peninsularis*, *L. longistylus* [1], *D. rariflora* [10] and *D. floribunda* [5]) and 3-phenyl-4-hydroxycoumarins (*D. robusta* [11], *D. scandens* [12] and *D. glabrescens* [13]).

The taxonomic revision of genera *Derris* and *Lonchocarpus*, on a worldwide basis, is badly needed. Our study, especially when extended to other species, may contribute to a better knowledge of the status of these two related genera and permit the sorting out of species on a more rational basis. The nomenclature of South American species is in accordance with Krukoff and Smith's paper [15] (see also [16]).

EXPERIMENTAL

Plant material. 8 g *L. xuul* Lundell (Dwyer 12399) from Belize; 9.3 g *L. unifolius* Benth (R. Cedillo, J. Calzada 179) from Mexico; 10 g *L. capassa* Rolfe (Dr. Fanshaw s.n. (Krukoff Herbarium 1974/10) from Zambia; 7.6 g *L. capassa* Rolfe (Th. Müller 1974/15) from Rhodesia; 12.9 g *L. capassa* Rolfe (Nat. Bot. Garden-Kirstenbosh s.n. (1975/3) from South Africa; 15 g *L. sericeus* Hatch, Greenw. (Faden 74/9, MO 74243) from Ghana; 10 g *L. peninsularis* (Dr. Janzen) from Costa Rica; 3.5 g *L. eriocaulinalis* from South America. The first 6 samples of 4 spp. were obtained from B. A. Krukoff's collections and they are backed by herbarium material in various institutions. The last 2 samples were supplied by Prof. E. A. Bell and the voucher is present in the Kew herbarium.

Extraction and separation. Seeds were powdered and continuously extracted with hot MeOH. The extract was decanted

from an oil (triglycerides) and evapd. The residue was dissolved in CHCl₃ and filtered from insoluble material (positive ninhydrin for amino acids) and the soln evapd. The crude extract was chromatographed on Si gel and the column was eluted with C₆H₆ and C₆H₆-EtOAc mixtures.

3-hydroxyisolonchocarpin 11. Crystals from MeOH mp 161-2° (Found: C, 74.40; H, 5.73. C₂₀H₁₈O₄ requires: C, 74.52; H, 5.63%). UV $\lambda_{\text{MeOH}}^{\text{max}}$ nm (log ϵ): 264 (4.26), 300 sh (3.86). PMR (60 MHz, CDCl₃): δ 7.7 (1H, d, J = 9 Hz, H-5), 7.6-7.3 (5H, m, C₆H₅-), 6.6 (1H, d, J = 10 Hz, H- α), 6.45 (1H, d, J = 9 Hz, H-6), 5.5 (1H, d, J = 10 Hz, H- β), 5.06 (1H, d, J = 12 Hz, H-2), 4.46 (1H, d, J = 12 Hz, H-3), 3.7 (1H, exchangeable with D₂O, OH), 1.23 (6H, s, gem-dimethyls). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3600, 1680.

In *L. eriocaulinalis* 2 other flavanones were present. The small amount of plant material (3.5 g) made purification and identification of these minor components impossible.

REFERENCES

1. Delle Monache, F., Marletti, F., Marini-Bettolo, G. B., De Mello, J. F. and De Lima, O. G. (1977) *Lloydia* 40, 201.
2. Delle Monache, G., De Mello, J. F., Delle Monache, F., Marini-Bettolo, G. B. and De Lima, O. G. (1975) *Il Farmaco Ed. Sci.* 30, 326 and refs. cited therein.
3. Pelter, A. and Amenechi, P. I. (1969) *J. Chem. Soc. (C)*, 887.
4. Dean, F. M. (1963) in *Naturally Occurring Oxygen Ring Compounds*, p. 501. Butterworth, London.
5. Braz Filho, R., Gottlieb, O. R., Murão, A. P., Da Rocha, A. T. and Oliveira, F. S. (1973) *Phytochemistry* 14, 1454.
6. Delfel, N. and Tallent, W. H. (1969) *J. AOAC* 52, 182.
7. Do Nascimento, M. C., De Vasconcelos Dias, R. L. and Mors, W. B. (1976) *Phytochemistry* 15, 1553.
8. Do Nascimento, M. C., and Mors, W. B. (1972) *Phytochemistry* 11, 3023.
9. Harper, S. H. and Underwood, W. G. E. (1965) *J. Chem. Soc.*, 4203 and refs. cited therein.
10. Braz Filho, R., Gottlieb, O. R. and Murão, A. P. (1975) *Phytochemistry* 14, 261.
11. Ollis, W. D., East, A. J. and Wheeler, R. E. (1969) *J. Chem. Soc.*, 365.
12. Ollis, W. D., Falshaw, C. P., Harmer, R. A., Wheeler, R. E., Lalitha, V. R. and Subbarao, N. V. (1969) *J. Chem. Soc.* 374.
13. Delle Monache, F., Cairo Valera, G., Sialer de Zapata, D. and Marini-Bettolo, G. B. (1977) *Gazz. Chim. Ital.* 107, 403.
14. Chopin, J. and Dumas, P. (1965) *Bull. Soc. Chim. France*, 3350.
15. Krukoff, B. A. and Smith, A. C. (1937) *Am. J. Botany* 24, 573.
16. Panshin, A. J. (1937) *Am. J. Botany* 24, 587.