Phytochemistry, 1972, Vol. 11, pp. 3023 to 3028. Pergamon Press. Printed in England.

CHALCONES OF THE ROOT BARK OF *DERRIS SERICEA*

MARIA CÉLIA DO NASCIMENTO and W. B. MORS
Centro de Pesquisas de Produtos Naturais, Faculdade de Farmácia, UFRJ, Rio de Janeiro ZC-82, Brazil

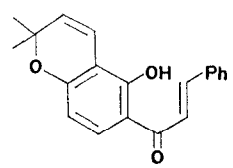
(*Revised Received* 1 *May* 1972. *Accepted* 18 *May* 1972)

Key Word Index—*Derris sericea*; Leguminosae; chalcones; flavanones; NMR and MS spectra.

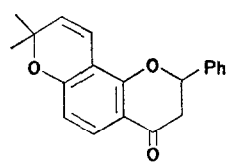
Abstract—In addition to two chalcones and one flavanone previously isolated from the root bark of *Derris sericea*, a third chalcone, derricidin, has been found and its structure determined (III). Cyclization of this, and of the already known derricin (II), to the corresponding flavanones was accomplished. The almost, but not completely, identical fragmentation of such chalcone–flavanone pairs in the mass spectrometer is discussed and interpreted. NMR data, which contribute decisively to structure elucidation, are also presented.

INTRODUCTION

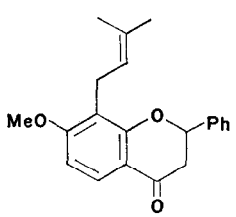
Derris sericea (H.B.K.) Ducke (syn. *Lonchocarpus sericeus* H.B.K.) is a tree of the Leguminosae, subfamily Lotoideae, native to northeastern Brazil,[1] but also well represented in western Africa, where it was introduced as an ornamental.[2] The chalcone, lonchocarpin (I), was isolated from its root by Baudrenghien *et al.* in 1949,[3] and the correct structure assigned to the compound by the same workers in 1953.[4]



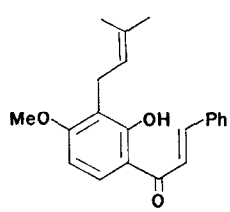
(I) Lonchocarpin



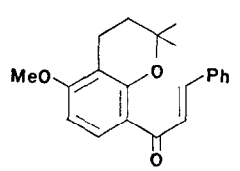
(Ia) Isolonchocarpin



(IIa) Isoderricin A



(II) Derricin

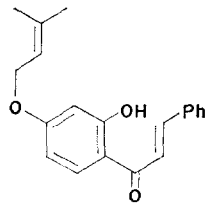


(IIb) Isoderricin B

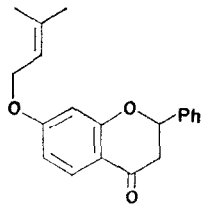
In a recent study,[5] the present authors described a second chalcone, derricin (II), accompanying lonchocarpin (I) in the root bark of *D. sericea*. Isolonchocarpin (Ia), the flavanone corresponding to lonchocarpin, was also detected in the same material. This flavanone had previously been obtained by isomerization of lonchocarpin in the laboratory.[4]

[1] A. DUCKE, *An. Acad. Brasil. Ciênc.* **31,** 274 (1959).
[2] A. CHEVALIER, *Rev. Bot. Appl.* **11,** 633 (1931).
[3] J. BAUDRENGHIEN, J. JADOT and R. HULS, *Bull. Soc. Roy. Sci. Liège* **18,** 52 (1949).
[4] J. BAUDRENGHIEN, J. JADOT and R. HULS, *Bull. Acad. Roy. Belg.* **39,** 105 (1953).
[5] M. C. NASCIMENTO and W. B. MORS, *An. Acad. Brasil. Ciênc.* **42** (Supl.), 87 (1970).

An earlier attempt to cyclize derricin (II) to the corresponding flavanone (IIa) was unsucessful; instead, cyclization under acidic conditions produced the alternative chromane, IIb.[5] However, it has now been possible to cyclize III in alkaline conditions, to the flavanone, IIa. The structure of a third chalcone, derricidin (III), extracted from the same material, has also been established, and this, in turn, has been cyclized in acid to the corresponding flavanone, isoderricidin (IIIa), in rather low yield.



(III) Derricidin

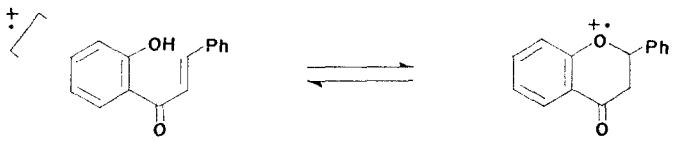


(IIIa) Isoderricidin

RESULTS

Mass Spectral Comparison of Chalcones and Their Corresponding Flavanones

At the beginning, it was discovered that the pairs of isomers lonchocarpin (I) and isolonchocarpin (Ia), and derricin (II) and isoderricin-A (IIa), gave almost identical MS. In the end, however, this fact actually proved to be an aid in identification. The literature shows that mass spectral fragmentation of chalcones and their corresponding flavanones leads to almost identical spectra.[6,7] For a proper interpretation of these fragments, an equilibrium between the two ionized forms is assumed to occur (II):



For the new pair of compounds, derricin-isoderricin A, the fragmentation can be drawn as shown in Scheme 1. More careful comparison shows that the mass spectral fragmentations of chalcones and flavanones are not completely identical. In fact, there is a marked difference

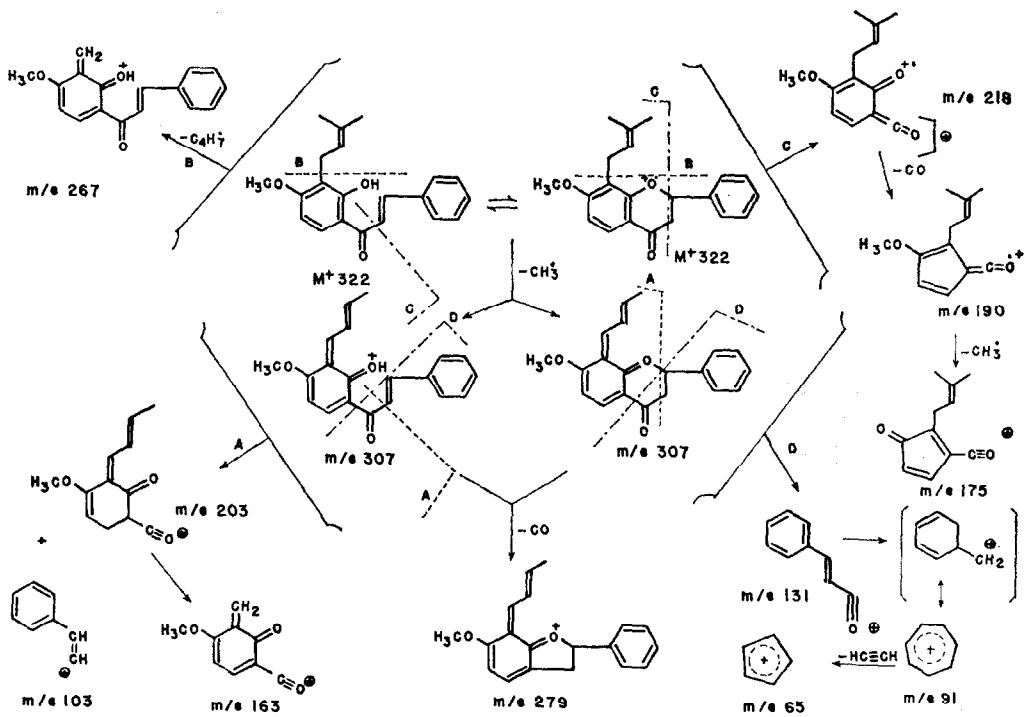
TABLE 1. RELATIVE INTENSITY OF MASS FRAGMENTATION PEAKS OF DERRICIN AND ISODERRICIN A (%)

m/e	Derricin	Isoderricin A	*m/e*	Derricin	Isoderricin A
77	8	25	190	9	100
103	28	20	203	24	63
131	46	24	218	5	98
163	70	50	267	48	17
175	15	95	279	100	51
			307	8	21

in the relative intensity of some peaks, which indicates that the equilibrium between the two forms is not complete. For some fragments the flavanone shows a much stronger intensity than the chalcone, as exemplified in Table 1 for the pair derricin-isoderricin A.

[6] H. BUDZIKIEWICZ, C. DJERASSI and D. H. WILLIAMS, *Structural Elucidation of Natural Products by Mass Spectrometry*, Vol. II, p. 258, Holden-Day, San Francisco (1964).
[7] A. P. JOHNSON, A. PELTER and P. STAINTON, *J. Chem. Soc.* 192 (1966).

In some instances, the difference in intensity is particularly striking. The peak *m/e* 218 is almost absent in the spectrum of derricin. The weakness of *m/e* 190 and 175 indicates that they derive in turn from *m/e* 218. Thus it seems as if the flavanone is more prone to fragmentation, allowing for a more precise interpretation of the spectrum. The loss of CO, a very stable neutral particle, favors the base peak of the chalcone at *m/e* 279, whereas in the case of the flavanone only 50% favors this same fragmentation. Elimination of a methyl group from the molecular ion ($M-CH_3$) derives from the side chain in both molecules.[6] But the loss of CH_3 from a methoxyl group was observed almost only in the flavanone, where the corresponding peak *m/e* 175 reaches a relative intensity of 95%, against only 15% in the chalcone.



SCHEME 1. MS SPECTRAL FRAGMENTATION OF DERRICIN AND ISODERRICIN A.

The MS fragmentation of the other (irreversible) cyclization product of derricin, isoderricin B (IIb) is very distinct. The most important step is the fission of the dimethylchromane ring through the formal loss of the $C_4H_7^{\cdot}$ radical and subsequent elimination of styryl, resulting in the fragment *m/e* 163, which corresponds to the 100% base peak.[7] Some other important fragmentations include the loss of one methyl group, which in itself shows up with low intensity (*m/e* 307).

Derricidin (III)

Elemental analysis and MS of this yellow compound, m.p. 116°, indicate $C_{20}H_{20}O_3$ (MW 308). Strong absorption peaks in the IR region of 6–7 μ indicate an aromatic compound. A strong carbonyl appears at ν 1640 cm^{-1}, a displacement due to hydrogen bonding

TABLE 2. NMR DATA

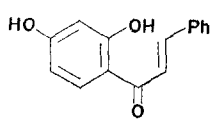
Group	Lonchocarpin	Isolonchocarpin	Derricin
Dimethylallyl	—	—	1·70(3H)
			1·80(3H)
2,2-Dimethylchromen	1·50(6H)	1·48(6H)	—
	5·50(1H)	5·60(1H)	—
	6·78(1H)	6·70(1H)	—
Methoxyl	—	—	3·82(3H)
2,2-Dimethylchroman	—	—	—
	—	—	—
	—	—	—
Styryl	7·20(1H)	—	7·20(1H)
	7·80(1H)	—	7·80
Methylene	—	2·92(2H)	3·40(2H)
Hydroxyl	13·2(1H)	—	13·32(1H)
Aromatic	6·20–6·50(1H)	6·70–7·10(1H)	6·60(1H)
	7·60–8·10(1H)	8·05(1H)	7·60–8·15(1H)
	6·50–7·60(5H)	7·48(5H)	6·60–7·60(5H)
Isolated protons	—	5·50(1H)	5·24(1H)

* All data in δ units, with spectra scanned up to $\delta = 16$; solvent $CDCl_3$, with Me_4Si as internal standard ($\delta = 0$).

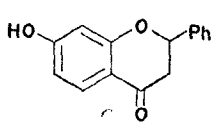
with the hydroxyl group in favorable position. Absorption due to in-plane vibration of skeletal C=C can be located at ν 1450 cm^{-1}. Strong peaks at ν 770, 750 and 590 cm^{-1} identify the five protons of the phenyl ring. Another strong absorption at ν 970 cm^{-1} indicates the presence of a *trans* double bond; a *gem*-dimethyl grouping next to a double bond absorbs characteristically at ν 1360 cm^{-1}, together with a weak doublet, at approx. 1360 and 1380 cm^{-1}, due to symmetric and asymmetric C–CH_3 stretching vibrations. A medium strong band at 1650 cm^{-1} corresponds to a methylene next to a double bond and to an oxygen atom.[5]

The UV spectrum shows a bathochromic shift in alkali, indicating that it is phenolic. NMR data (Table 2) show that derricidin has structure III. The mass spectrum is also entirely in accord with structure III. An interesting fragmentation is the loss of 68 m.u. through elimination of the dimethylallyl ether substituent, leading to the 100% base peak at *m/e* 240. There is also loss of styryl, clearly seen at *m/e* 103, and the rupture at the olefinic bond, leading to a peak *m/e* 163 (relative intensity 77%).

Additional information in favor of III was obtained by acid cyclization to its corresponding flavanone (IIIa).[5]



(IV)



(IVa)

Acid treatment of III for a longer period (36 hr), instead of increasing the yield of flavanone, caused the loss of the isoprene sidechain. The NMR data show that an inseparable mixture of a new chalcone-flavanone pair (IV, IVa) is produced. Evidently, the new hydroxyl

OF PRENYLATED CHALCONES AND FLAVANONES*

Isoderricin A	Isoderricin B	Derricidin	Isoderricidin
1·6(6H)	—	1·78(6H)	1·60(6H)
—	—	—	—
—	—	—	—
—	—	—	—
2·88(3H)	3·87(3H)	—	—
—	1·38(6H)	—	—
—	2·70(2H)	—	—
—	1·82(2H)	—	—
—	7·20(1H)	7·20(1H)	—
—	7·80(1H)	7·80(1H)	—
			4·50(2H)
2·92(2H)	—	4·42(2H)	2·98(2H)
—	—	13·2(1H)	—
6·60(1H)	6·60(1H)	6·40(1H)	6·50(2H)
7·90(1H)	7·90(1H)	7·90(1H)	7·80(1H)
7·48(5H)	6·60–7·90(5H)	6·40–7·90(5H)	7·42(5H)
5·36(1H)	—	5·50(1H)	5·50(1H)
			6·20(1H)

in position 6′ favours the chalcone form, due to hydrogen bonding with the carbonyl group, and making free rotation of ring A and cyclization difficult. The difficulty of separating chalcone–flavanone pairs has already been pointed out by Neu.[8]

In addition to the flavonoids of *D. sericea*, an unidentified triterpene was also isolated. An aliphatic alcohol [MC-E (5)] was by MS found to be a mixture of cerylic and carnaubylic alcohols, with traces of $C_{24}H_{50}O$.

EXPERIMENTAL

M.ps were determined on the Kofler hot stage. UV spectra were obtained in 95% EtOH and IR spectra in KBr pellets. NMR spectra (60 MHz) were obtained with a Varian T60 instrument at the Instituto Nacional de Tecnologia, Rio de Janeiro. MS (70 eV) and NMR (100 MHz) were performed at the Department of Chemistry, Stanford University.

Extraction. The dried and ground root bark was first extracted exhaustively with cold hexane, then with cold ether. After evaporation, the residues were chromatographed on a column of silica-gel (E. Merck, 0·05–0·20 mm). Elution with solvent mixtures of increasing polarity yielded in succession: lonchocarpin, derricin, and isolonchocarpin (present in the ether extract only).[5]

Derricidin. This chalcone was in part eluted from the hexane extract, in part with hexane–benzene (2:1) (together with derricin), in part with EtOAc (without accompanying substances). Yellow crystals from EtOH, m.p. 116°. IR: ν_{max} 3005, 1640, 1620, 1450, 970, 750, 690 cm^{-1}. UV: max 342 nm (ϵ 24 000), 268 (ϵ 1850), 216 (ϵ 2300). MS: M^+ 308; fragments at *m/e* 69, 103, 137, 163, 239, 240. For NMR data, see Table 2.

Isoderricin A (cyclization of derricin). 200 mg derricin were dissolved in 2 ml EtOH and 4 ml aq. NaOH 1·5% added at the b.p. Heating was discontinued and the mixture left at room temp for 24 hr. Upon acidification, colorless crystals precipitated, which were filtered and recrystallized from EtOH. m.p. 123°. IR: (KBr), ν_{max} 3020, 1660, 1600, 1500, 1450, 945, 915, 985, 810, 770, 760, 730, 705 cm^{-1}. MS: see Table 1; NMR: see Table 2.

Isoderricidin (cyclization of derricidin). 80 mg of derricidin (III) were heated under reflux for 24 hr with 20 ml EtOH, 10 ml H_2O and 2 ml conc HCl. After cooling, colorless needles (8 mg) crystallized, which were recrystallized from EtOH. m.p. 189°, IR, ν_{max} 3020, 3010, 1660, 1520, 1455, 1175, 1105, 1060, 1010, 970, 895, 860, 810, 770, 760, 695 cm^{-1}. MS: M^+ 308 (*m/e* 8%); 241 (84%); 240 (78%), 239 (59%); 223 (38%); 212 (20%); 297 (20%); 163 (65%); 137 (100%); 136 (78%); 103 (99%); 78 (82%); 77 (76%); 69 (28%).

[8] R. Neu, *J. Chromatogr.* **4**, 489 (1960).

UV max 222 (ε 9476), 281 (ε 9055), 318 (ε 7700), 349 (ε 3819). min 230 (ε 8993), 254 (ε 4419), 304 (ε 7515), 385 (ε 616). NMR: α 1·66 (6H), 4·50 (2H), 2·98 (2H), 6·50 (2H), 7·80 (1H), 7·42 (5H), 5·50 (1H), 6·20 (1H).

Acid degradation of derricidin. 80 mg of derricidin (III) were heated under reflux, for 36 hr, with 20 ml EtOH, 10 ml H_2O and 2 ml conc HCl. After cooling, colorless needles (5 mg) crystallized, which were recrystallized from EtOH. The large melting interval (172–179°) indicated a mixture of IV and IVa, which was confirmed by the NMR spectrum (see text). TLC on silica-gel gave no resolution; the best solvent (hexane–benzene, 1:4) gave two almost coinciding spots, discernible only by fluorescence in UV light.

Acknowledgements—The authors gratefully acknowledge the financial support received from the Conselho Nacional de Pesquisas (National Research Council, Brazil); Coordenação do Aperfeiçoamento do Pessoal de Nível Superior (Agency for Training, Ministry of Education); Banco Nacional do Desenvolvimento Econômico (Brazilian Economic Development Bank); and Conselho de Pesquisas da UFRJ (Research Council of the Federal University of Rio de Janeiro). The authors thank Drs. Libero Antonaccio, Paul M. Baker, A. M. Duffield and L. J. Durham for help with the spectra, and the Microanalytical Laboratory of Dr. A. Bernhardt, Mülheim, Germany for the elemental analyses.