Acknowledgement—We thank the Department of Botany and Microbiology, Arizona State University, for partial financial support of this study.

REFERENCES

1. Pinkava, D. J., McLeod, M. G., McGill, L. A. and Brown, R. C. (1973) *Brittonia* **25,** 2.
2. Nair, A. G. R. and Subramanian, S. S. (1961) *J. Sci. Ind. Res. Sect. B* **20,** 507.
3. Arcoleo, A., Ruccia, M. and Cusmano, S. (1961) *Ann. Chim.* (*Rome*) **51,** 751.
4. Arcoleo, A., Bellino, A. and Ruccia, M. (1961) *Atti Accad. Sci. Lett. Arti Palermo* **22,** 115.
5. Nair, A. G. R. and Subramanian, S. S. (1964) *Curr. Sci.* **33,** 211.
6. Rösler, H., Rösler, U., Mabry, T. J. and Kagan, J. (1966) *Phytochemistry* **5,** 189.
7. Shabbir, M. and Zaman, A. (1968) *J. Indian Chem. Soc.* **45,** 81.
8. Richardson, M. (1978) *Biochem. Syst. Ecol.* **6,** 283.
9. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids.* Springer, New York.
10. Harbone, J. B. (1973) *Phytochemical Methods,* p. 225. Chapman & Hall, London.
11. Clark, W. D. (1980) *Phytochem. Bull.* (in press).

Phytochemistry, 1980, Vol. 19, pp. 1857–1858. Pergamon Press Ltd. Printed in England.

DERRONE, A NEW PYRANOISOFLAVONE FROM *DERRIS ROBUSTA* SEEDS

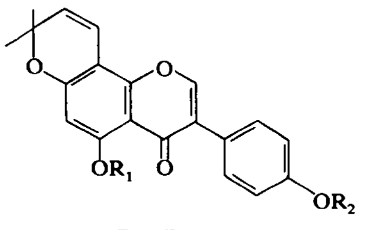
S. S. Chibber and R. P. Sharma

Department of Chemistry, University of Delhi, Delhi-110007, India

(*Received* 19 *November* 1979)

Key Word Index—*Derris robusta*; Leguminosae; derrone; 5,4′-dihydroxy-2″,2″-dimethylpyrano(5″,6″:7,8)-isoflavone.

In continuation [1] of our work on the seeds of *Derris robusta* we wish to report the isolation of a new pyranoisoflavone, derrone, from the combined ethyl acetate and methanol extracts. It analysed for $C_{20}H_{16}O_5$ (M^+ 336). That derrone is an isoflavone containing a chelated hydroxyl was shown by absorption at 3400 and 1647 cm^{-1} in the IR spectrum, λ_{max}^{MeOH} 280 nm in the UV spectrum and by sharp singlets at δ13.80 (chelated hydroxyl) and 7.73 (H-2 of the isoflavones). Location of a chelated hydroxyl at position-5 is shown by a bathochromic shift of 9 nm with $AlCl_3$ in UV. Absence of a shift [2] with NaOAc in the UV spectrum indicated the absence of a free hydroxyl at position-7. The presence of two hydroxyls in derrone was shown by the NMR of its acetate which exhibited two singlets at δ2.44 and 2.30, each integrating for three protons. NMR of the compound showed a six-proton singlet at δ1.42, assignable to a gem-dimethyl group and two doublets ($J = 10$ Hz) at 6.68 and 5.56, integrating for one proton each, corresponding to vinylic protons (H-4″ and H-3″, respectively) suggesting the presence of a 2,2-dimethylchromen residue [3]. Two doublets ($J = 9$ Hz) at δ7.29 and 6.77, each integrating for two protons, characteristic of A_2B_2 pattern, in the NMR of the compound were attributed to the 2′,6′- and 3′,5′-protons respectively. The other hydroxyl is, therefore, assigned to the 4′-position which is evidenced by peaks at *m/e* 203(5%) and 118(3%) (arising from retro-Diels–Alder fission of the M − 15 ion) in the MS [4] of the compound. That the 2,2-dimethylchromen residue is at the 7,8-position in derrone was established by a negative Gibb's test and by comparing the chemical and spectral data of its monomethyl ether with that reported in literature [5]. Therefore, a sharp singlet at δ 6.27 was assigned to H-6. Hence derrone is 5,4′-dihydroxy-2″,2″-dimethylpyrano(5″,6″:7,8)isoflavone (**1**).



1 $R_1 = R_2 = H$
2 $R_1 = H, R_2 = Me$
3 $R_1 = R_2 = Ac$

EXPERIMENTAL

^{1}H NMR spectra were taken at 90 MHz in $CDCl_3$ and chemical shifts are given in δ (ppm) scale relative to TMS; UV spectra were obtained in MeOH and IR spectra as KBr discs.

Isolation. Air-dired and coarsely powdered seeds (240 g) were successively extracted with hot petrol (bp 60–80°), C_6H_6, EtOAc and MeOH. The EtOAc and MeOH extracts were found to be similar (TLC) and hence combined and subjected to column chromatography over Si gel. On elution with C_6H_6–EtOAc (9.3 : 0.7), a crystalline compound (30 mg) was obtained. TLC: R_f 0.15 ($CHCl_3$–EtOAc, 9 : 1); mp 216–218°; λ_{max}^{MeOH} nm: 280, 359 sh; +NaOAc 280, 359 sh; +$AlCl_3$ 289, 365. ν_{max}^{KBr} cm^{-1}: 3400 and 1647. ^{1}H NMR ($CDCl_3$): δ 1.42 (*s*, 6H, gem-dimethyl group), 5.56 (*d*, $J = 10$ Hz, 1H, H-3″), 6.27 (*s*, 1H, Ar-$\underline{H}_6$), 6.68 (*d*, $J = 10$ Hz, 1H, H-4″), 6.77 (*d*, $J = 9$ Hz, 2H, Ar-$\underline{H}_{3'}$ and Ar-$\underline{H}_{5'}$), 7.29 (*d*, $J = 9$ Hz, 2H, Ar-$\underline{H}_{2'}$ and Ar-$\underline{H}_{6'}$), 7.73 (*s*, 1H, H-2) and 13.80 (*s*, 1H, chelated hydroxyl). MS (*m/e*, %): 336 (M^+, 18), 322 (21), 321 ($M^+ -$ Me, 100), 203 (5), 160.5 (12), 152 (4) and 118 (3).

Acetylation of derrone (15 mg) (Ac_2O–Py) gave the diacetate (**3**) as needles (15 mg), mp 225–227°. ^{1}H NMR ($CDCl_3$): δ 1.48 (*s*, 6H, gem-dimethyl group), 2.30, 2.44 (each *s*, 2×3H, $2 \times$ O-CO$C\underline{H}_3$), 5.8 (*d*, $J = 10$ Hz, 1H, $\underline{H}$-3″), 6.53 (*d*, $J = 10$ Hz, 1H, H-4″), 6.73 (*s*, 1H, Ar-$\underline{H}_6$), 7.18 (*d*, $J = 9$ Hz, Ar-$\underline{H}_{3'}$ and Ar-$\underline{H}_{5'}$), 7.51 (*d*, $J = 9$ Hz, Ar-$\underline{H}_{2'}$ and Ar-$\underline{H}_{6'}$) and 7.81 (*s*, 1H, H-2).

Methylation of derrone (10 mg) by diazomethane gave a monomethyl ether as needles (10 mg) mp 170–172°, characterized as 5-hydroxy-4′-methoxy-2″,2″-dimethylpyrano-(5″,6″:7,8)isoflavone (**2**) by comparing its chemical (mp, mmp, co-TLC) and spectral (UV, IR, NMR) data with that reported in literature [5].

REFERENCES

1. Chibber, S. S. and Sharma, R. P. (1980) *Indian J. Chem.* (in press).
2. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, p. 169. Springer, Berlin.
3. Schwarz, J. S. P., Cohen, A. I., Ollis, W. D., Kaczka, E. A. and Jackman, L. M. (1964) *Tetrahedron* **20,** 1317.
4. Barnes, C. S. and Occolowitz, J. L. (1964) *Aust. J. Chem.* **17,** 975.
5. Jackson, B., Owen, P. J. and Scheinmann, F. (1971) *J. Chem. Soc.* C 3389.