Tetrahedron Letters No.49, pp. 4451-4455, 1965. Pergamon Press Ltd.
Printed in Great Britain.

DALBERGIA SPECIES - III

D.M.X. Donnelly, M. R. Geoghegan and B. J. Nangle

Department of Chemistry, University College,

Dublin, Ireland,

and

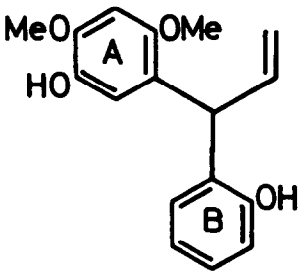
R. A. Laidlaw,

Forest Products Research Laboratory,

Princes Risborough, England.

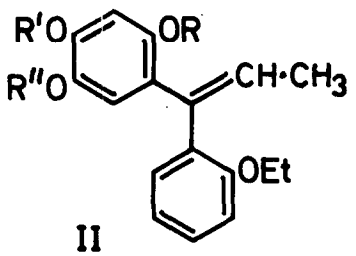
(Received 8 October 1965)

A recent publication (1) which established the position of the hydroxyl groups in latifolin (2,3) prompts us to report our work on this problem. Latifolin together with (R)-dalbergione (4,5), 2,4,6-trimethoxyacetophenone, β-sitosterol (6) and dalbergin (7), was isolated from Dalbergia latifolia. Latifolin (I) showed a negative plain optical rotatory dispersion curve.

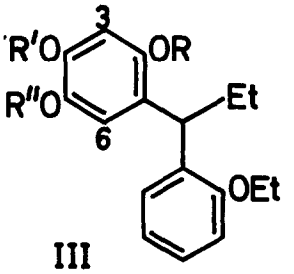


I

Oxidation of latifolin diethyl ether with potassium permanganate yielded o-ethoxybenzoic acid and established that one of the hydroxyl groups was at position 2' in the B-ring. A comparison of the propenes (IIa, b,c,) and the diethyl ether of isolatifolin (IV) and the propanes (IIIa, b,c,) with dihydrodiethyl latifolin (racemic) located the second hydroxyl group at position 5 in Ring A.

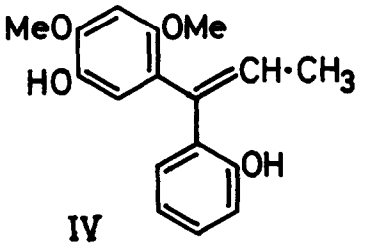


II



III

a R = Et, R' = R'' = Me
b R' = Et, R = R'' = Me
c R'' = Et, R = R' = Me



IV

4,2'-Diethoxy-2-5,dimethoxybenzophenone and 5,2'-diethoxy-2,4-dimethoxybenzophenone were prepared by Friedel-

Crafts acylation of the respective ethoxymethoxybenzenes (1 mole) with o-ethoxybenzoyl chloride (1 mole). A short reaction time (10 min.) prevented the occurrence of dealkylation. Reaction of 1,3,4-trimethoxybenzene (1 mole) with o-ethoxybenzoyl chloride (1 mole) gave 2-hydroxy-2'-ethoxy-4,5-dimethoxybenzophenone which on ethylation gave 2,2'-diethoxy-4,5-dimethoxybenzophenone. The propenes (IIa, b,c,) were obtained by treatment of the corresponding benzophenones with ethyl magnesium iodide and subsequent dehydration using ethanolic sulphuric acid. Hydrogenation with Adam's catalyst in methanol gave the propanes (IIIa, b,c,).

Table I summarises the physical, spectral and analytical data for the benzophenones, propenes (IIa, b,c,) propanes (IIIa, b,c,), isolatifolin diethyl ether and latifolin dihydrodiethyl ether (racemic).

For comparison, latifolin was isomerised with aqueous potassium hydroxide (66%) to give isolatifolin (IV) m.p. 105° $[\alpha]_D^{21^\circ} \pm 0.00^\circ$. The N.M.R. spectrum showed a doublet 8.37 τ and quartet 4.01 τ (J=7 c.p.s.) corresponding to the group $\rangle C = CH\text{-}CH_3$. Ethylation of isolatifolin gave a diethyl ether m.p. 79° undepressed on admixture with 1-(2,4-dimethoxy-5-ethoxyphenyl)-1-(2-ethoxyphenyl)prop-1-ene (IIc). Hydrogenation of isolatifolin diethyl ether gave the dihydro compound identical with propane (IIIc).

TABLE I

Compounds	m.p. [lit] (°C)	Spectral data	Elemental Analysis
2,2'-diethoxy-4,5-dimethoxy benzophenone	105-106	1653 cm^{-1}	F: C 69.0, H 6.9 OMe 18.8, OEt 27.3
4,2'-diethoxy-2,5-dimethoxy benzophenone	117.5-118	1653 cm^{-1}	F: C 69.1, H 6.8 OMe 18.4, OEt 26.8
5,2'-diethoxy-2,4-dimethoxy benzophenone	91-92 [93]	1653 cm^{-1}	F: C 69.0, H 6.74 OMe 18.6, OEt 26.7 C: C 69.1, H 6.7 OMe 18.8, OEt 27.2
Propene II			
a	98-99		F: C 73.3, H 7.4
b	78.5-79		F: C 73.7, H 7.54
c	79-79.5 [82-83]		F: C 74.0, H 7.6 C: C 73.6, H 7.7
Propane III		H_3 H_6	
a	61-61.5	3.48τ 3.15τ	F: C 73.3, H 8.3
b	64-65	3.9τ 3.7τ	F: C 73.2, H 8.19
c	51-52.5	3.47τ 3.2τ	F: C 73.3, H 8.16 C: C 73.2, H 8.14
Isolatifolin diethyl ether	78-79 [83]		F: C 74.0, H 7.6 C:C73.6, H 7.7
Latifolin dihydro-diethyl ether (racemic)	51.5-52.5		F: C 73.3, H 8.1 OMe 18.3, OEt 26.4 C: C 73.2, H 8.14 OMe 18.0, OEt 26.2

Acknowledgment. We are indebted to Professor E. M. Philbin for her interest and encouragement, Professor W. Klyne for the O.R.D. curves, Professor V. Prelog (Zurich) and Dr. R. C. Pink (The Queen's University of Belfast) for N.M.R. spectra and the Minister of Education, Republic of Ireland, for award of a Maintenance Grant (to B.J.N.).

References

1. D. Kumari, S. K. Mukerjee and T. R. Seshadri, Tetrahedron, 21, 1495 (1965).
2. S. Balakrishna, M. M. Rao and T. R. Seshadri, Tetrahedron, 18, 1503 (1962).
3. C. B. Dempsey, D. M. X. Donnelly and R. A. Laidlaw, Chem. and Ind., 491 (1963).
4. W. B. Eyton, W. D. Ollis, I. O. Sutherland, L. M. Jackman, O. R. Gottlieb and M. T. Magalhaes, Proc. Chem. Soc., 301 (1962).
5. B. J. Donnelly, D. M. X. Donnelly and C. B. Sharkey, Phytochemistry, 4, 337 (1965).
6. Isolated from pet. ether (b.p. 60-80°) extract by B. J. Donnelly (unpublished result).
7. M. M. Rao and T. R. Seshadri, Tetrahedron Letters, 211 (1963).