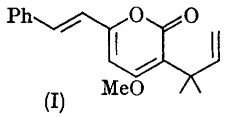
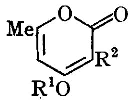
The Constitution and Synthesis of Mundulea Lactone

By M. C. MANGER, W. D. OLLIS,* and I. O. SUTHERLAND
(*Department of Chemistry, The University, Sheffield,* 10)

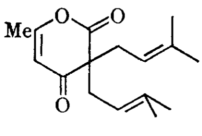
RECENTLY the constitution (I) was tentatively assigned[1] to a yellow compound called mundulea lactone isolated[2] from an Indian sample of *Mundulea sericea* (syn. *Mundulea suberosa*). This structural proposal (I) was based mainly upon spectroscopic evidence and involved an unusual interpretation of nuclear magnetic resonance spectral data.[1] In view of our interest in the extractives of *M. sericea*[3] and that the constitution (I) involved the novel association of the relatively unusual αα-dimethylallyl group[4] with the natural 6-styryl-α-pyrone structural type,[5] the synthesis of mundulea lactone was undertaken to confirm the structural assignment.



(I)



(II) R^1=$Me_2C{:}CH{\cdot}CH_2$, R^2=H
(III) R^1=H, R^2=$Me_2C{:}CH{\cdot}CH_2$
(V) R^1=H, R^2=$CH_2{:}CH{\cdot}CMe_2$
(VI) R^1=Me, R^2=$CH_2{:}CH{\cdot}CMe_2$



(IV)

Alkylation of the monosodium salt of 4-hydroxy-6-methyl-2-pyrone[6] (triacetic acid lactone) with 3,3-dimethylallyl bromide in dimethyl sulphoxide gave the required 4-(3′,3′-dimethylallyloxy)-6-methyl-2-pyrone (II), m.p. 56°, together with the products (III), m.p. 112°, and (IV), m.p. 60°, resulting from *C*-alkylation. The dimethylallyl ether (II) was smoothly converted into 3-(1′,1′-dimethylallyl)-4-hydroxy-6-methyl-2-pyrone (V), m.p. 131°, by heating a solution of (II) in dimethyl sulphoxide at 120°. The isolation of a *single* product (V) in high yield (72%) from this reaction in dimethyl sulphoxide contrasts with results obtained from the high-temperature thermal Claisen rearrangement of other 3,3-dimethylallyloxy-derivatives,[7] but is analogous to the successful synthesis of 2-hydroxy-3-(1′,1′-dimethylallyl)-1,4-naphthoquinone by the Claisen rearrangement of 2-(3′,3′-dimethylallyloxy)-1,4-naphthoquinone[8] in boiling ethanol. Reaction of the hydroxy-pyrone (V) with diazomethane[9] gave a mixture of the 2- and 4-methyl ethers, whereas methylation with dimethyl sulphate–potassium carbonate in acetone gave exclusively the required 4-methyl ether (VI) which by magnesium methoxide catalysed condensation with benzaldehyde gave the 6-styryl-2-pyrone (I), m.p. 104°, identical[†] with the natural product.[‡] All new compounds had spectra and analyses in accord with the assigned structures.

Further studies of the Claisen rearrangement in dimethyl sulphoxide solution are in progress.

(*Received, April 27th,* 1967; *Com.* 403.)

[†] We thank Professor N. V. Subba Rao (Osmania University, Hyderabad) for a sample of natural mundulea lactone.

[‡] The reported n.m.r. spectrum of mundulea lactone (see ref. 1) is not compatible with the assigned structure (I), but this appears to be the result of an error of interpretation. The vinyl protons of the 1,1-dimethylallyl group appear as an ABX system ($\tau_A = 5\cdot08$, $\tau_B = 5\cdot14$, $\tau_X = 3\cdot78$; $J_{AB} = 1\cdot5$, $J_{AX} = 17\cdot5$, $J_{BX} = 10$ c./sec.), and the olefinic protons of the styryl residue appear as an AB system ($\tau_A = 2\cdot49$, $\tau_B = 3\cdot43$; $J_{AB} = 16$ c./sec.).

[1] V. R. Lalitha, G. Srimannarayana, and N. V. Subba Rao, *Current Sci.*, 1966, **35**, 410.

[2] K. B. Rao and N. V. Subba Rao, *J. Sci. Ind. Res. (India)*, 1958, **17**, *B*, 384.

[3] B. F. Burrows, N. Finch, W. D. Ollis, and I. O. Sutherland, *Proc. Chem. Soc.*, 1959, 150; N. Finch and W. D. Ollis, *Proc. Chem. Soc.*, 1960, 176; B. F. Burrows, W. D. Ollis, and L. M. Jackman, *Proc. Chem. Soc.*, 1960, 177; W. D. Ollis, "Symposium on Phytochemistry," September 1961, Hong Kong University Press, 1964, p. 128; S. F. Dyke, W. D. Ollis, and M. Sainsbury, *Proc. Chem. Soc.*, 1963, 179; *J. Chem. Soc.*, 1966, 749.

[4] W. D. Ollis and I. O. Sutherland, "Recent Developments in the Chemistry of Natural Phenolic Compounds," ed. W. D. Ollis, Pergamon, Oxford, 1961, p. 74.

[5] W. B. Mors, M. T. Magalhães, and O. R. Gottlieb, *Fortsch. Chem. org. Naturstoff.*, 1962, **20**, 131; F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworths, London, 1963, pp. 99–102.

[6] J. Collie, *J. Chem. Soc.*, 1891, 612.

[7] E. D. Burling, A. Jefferson, and F. Scheinmann, *Tetrahedron*, 1965, **21**, 2653; E. D. Burling, A. Jefferson, and F. Scheinmann, *Tetrahedron Letters*, 1964, 599; A. Jefferson and F. Scheinmann, *Tetrahedron Letters*, 1964, 1289.

[8] R. G. Cooke, *Austral. J. Sci. Res.*, 1950, *A*, **3**, 481.

[9] D. Herbst, W. B. Mors, O. R. Gottlieb, and C. Djerassi, *J. Amer. Chem. Soc.*, 1959, **81**, 2427; J. D. Bu'Lock and H. G. Smith, *J. Chem. Soc.*, 1960, 502.