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# SYNTHESIS OF LUCERNOL AND SATIVOL DIMETHYLETHER

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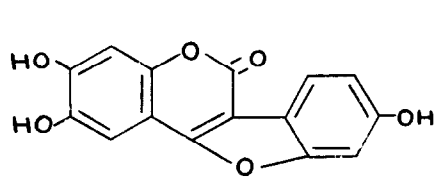
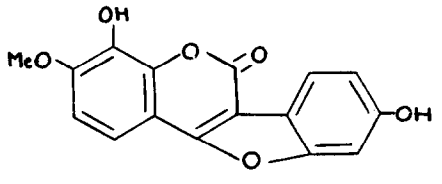
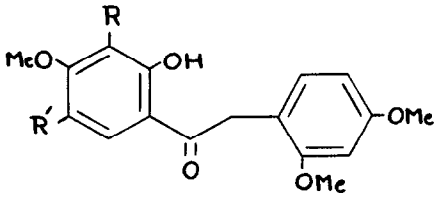
Lucernol (I) and sativol (II), the two new coumestans isolated recently from alfalfa by Bickoff et al. (1) along with twelve other phenolic compounds have been assigned structures on the basis of degradative and spectral studies. We now report the synthesis of lucernol and sativol-dimethyl ether.



I

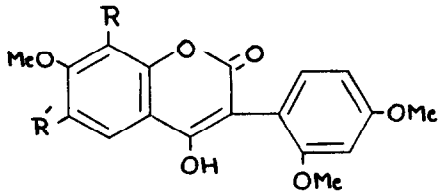


II



III, R=H ; R′=OMe

V, R=OMe ; R′=H



IV, R=H ; R′=OMe

VI, R=OMe ; R′=H

2-Hydroxy-4,5-dimethoxyphenyl-2,4-dimethoxybenzylketone (III) a key intermediate in the synthesis of lucernol was prepared by the following route. Friedel and Crafts reaction of 2,4-dimethoxyphenylacetylchloride with 1,2,4-trimethoxy benzene gave a mixture of 2-methoxy and hydroxyketones. The partial demethylation was completed by refluxing with $AlCl_3$ in $CH_3CN$ (½ hr) yielding the required 2-hydroxy ketone (III) as colourless needles from ethanol, m.p. 122-23°. Cyclisation by the ethylchloroformate method gave 6,7,2',4'-tetramethoxy-3-phenyl-4-hydroxycoumarin (IV) as colourless needles

from ethanol, m.p. 238-39°. Demethylative ring closure with HI (bath temp 170°) for 2 hr. in $CO_2$ atm. yielded a product which was purified by dissolution in aqueous borax and reprecipitation. It crystallised from methanol as buff-coloured needles, m.p. $> 350°$. Its purity was established by T.L.C. and paper chromatography. It was identical with an authentic sample of natural lucernol in T.L.C., paper chromatography, spectra and m.m.p. The triacetate and trimethyl ether of the synthetic lucernol agreed with those obtained from the natural sample in T.L.C., spectra and m.m.p.

2-Hydroxy-3,4-dimethoxyphenyl-2,4-dimethoxybenzyl ketone (V) (2) was cyclised with ethylchloroformate to 7,8,2',4'-tetramethoxy-3-phenyl-4-hydroxy coumarin (VI), as colourless needles from ethanol m.p. 178-79°. Demethylative ring closure with HI (bath temp 100°) for 5 min. yielded a mixture which on methylation with dimethyl sulphate, $K_2CO_3$ and acetone and crystallisation from methanol gave sativol dimethyl ether, m.p. 209-210° identical in chromatographic behaviour and spectra with the dimethyl ether of natural sativol; mixed m.p. was undepressed.

Acknowledgments

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## REFERENCES

1. R.R. Spencer, E.M. Bickoff, R.E. Lundin and B.E. Knuckles, J. Agri. Food Chem. 14, 162 (1966).
2. V.K. Kalra, A.S.Kukla and T.R. Seshadri, Tetrahedron (in Press).