

TPN<sup>+</sup> plus g-6-p. Magnesium ions are stimulatory. The reaction is a linear function of time over the interval 15 to 120 minutes.

The absolute requirement for ATP suggested that 3'-phosphoadenosine-5'-phosphosulfate (PAPS) might serve as substrate for the sulfate reductase, since previous studies had demonstrated the presence of the sulfate activating system in yeast.<sup>10,11</sup> Incubation of 0.1  $\mu$ mole of S<sup>35</sup>-PAPS with the sulfate reducing system (Table I, 1/5th scale) in the absence of ATP yielded 0.5  $\mu$ mole of S<sup>35</sup>O<sub>2</sub> although 1.9  $\mu$ moles was formed from an equivalent amount of S<sup>35</sup>O<sub>3</sub> (0.1  $\mu$ mole) and ATP (0.2  $\mu$ mole). S<sup>35</sup>O<sub>2</sub> was not formed from S<sup>35</sup>-PAPS in the absence of living enzyme, even with reduced TPN.

(10) R. S. Bandurski, L. G. Wilson and C. L. Squires, *THIS JOURNAL*, **78**, 6408 (1956).

(11) P. W. Robbins and F. Lipmann, *ibid.*, **78**, 6409 (1956).

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### THE STRUCTURE OF THE DESAURINS

Sir:

The desaurins form a class of stable, high-melting, neutral, yellow compounds obtainable most readily by the reaction of certain ketones with base and carbon disulfide; structure I was suggested for the prototype, the desaurin from deoxybenzoin.<sup>1</sup> Although this proposal subsequently was accepted,<sup>2</sup> it is without experimental support. Such a structure would have considerable interest both in sulfur and in small-ring chemistry. We now report the substantiation of this type of structure for two desaurins.

The desaurin from phenylacetone was obtained as lemon yellow needles, m.p. 233–233.5°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  6.05  $\mu$ ,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  246 m $\mu$  (log  $\epsilon$  3.96), 374 m $\mu$  (log  $\epsilon$  4.44) (*Anal.* Calcd. for C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub>: 2 C—CH<sub>3</sub>, 8.53; mol. wt., 352. Found: C—CH<sub>3</sub>, 7.34; mol. wt., 355).<sup>3</sup> Reduction with zinc and base gave two equivalents of 3-phenyl-2-butanone, establishing the presence of two C<sub>6</sub>H<sub>5</sub>—C—C—O residues.



The presence of two carbonyl functions was established by the formation of a *mono*-2,4-dinitrophenylhydrazone, deep red needles, m.p. 250–251°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  3.01, 6.05, 6.18, 6.27  $\mu$ ,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  356 m $\mu$  (log  $\epsilon$  4.37), 450 m $\mu$  (log  $\epsilon$  4.36), a *bis*-2,4-dinitrophenylhydrazone, purple brown powder, m.p. 285–286°.

(1) H. Bergreen, *Ber.*, **21**, 337 (1888); V. Meyer, *ibid.*, **21**, 353 (1888); **23**, 1571 (1890); V. Meyer and H. Wege, *ibid.*, **24**, 3535 (1891); W. Wachter, *ibid.*, **25**, 1727 (1892); P. Petrenko-Kritschenko, *ibid.*, **25**, 2239 (1892).

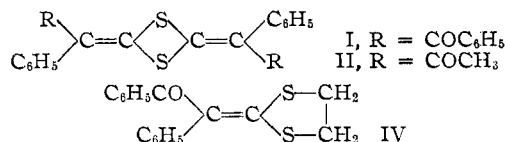
(2) C. Kelber, *ibid.*, **43**, 1252 (1910); C. Kelber and A. Schwarz, *ibid.*, **45**, 137 (1912).

(3) Satisfactory elemental analyses have been obtained for this and all other new compounds here described.

$\lambda_{\text{max}}^{\text{KBr}}$  3.06, 6.19, 6.32  $\mu$ ,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  260 m $\mu$  (log  $\epsilon$  4.26), 341 m $\mu$  (log  $\epsilon$  4.30), 505 m $\mu$  (log  $\epsilon$  4.34), and a dioxime, yellow needles, m.p. 209.5–210° dec.,  $\lambda_{\text{max}}^{\text{KBr}}$  3.00, 6.17  $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  250 m $\mu$  (shoulder, log  $\epsilon$  4.04), 267 m $\mu$  (shoulder, log  $\epsilon$  3.89), 347 m $\mu$  (log  $\epsilon$  4.31), 368 m $\mu$  (log  $\epsilon$  4.29); hydrolysis of the dioxime regenerated the desaurin, indicating the absence of gross structural change on derivatization. The desaurin gave a positive iodoform test and yielded with sodium hypochlorite an acid, C<sub>18</sub>H<sub>12</sub>O<sub>4</sub>S<sub>4</sub>, pale yellow microcrystals, m.p. 298–299° dec.,  $\lambda_{\text{max}}^{\text{KBr}}$  3.0–4.0, 6.02  $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  342 m $\mu$  (log  $\epsilon$  4.50), demonstrating that the carbonyl groups are present as two acetyl groups; this conclusion was corroborated by a strong band at 7.35  $\mu$  in the infrared and a single band at 1175 c.p.s.<sup>4</sup> in the n.m.r. spectrum of the desaurin. This evidence in conjunction with the infrared and ultraviolet spectral data requires the presence of two distinct C<sub>6</sub>H<sub>5</sub>CCOCH<sub>3</sub> groupings



and leads unambiguously to the structure II for the desaurin.<sup>5</sup>



The desaurin from deoxybenzoin, golden needles, m.p. 300–302° dec.,  $\lambda_{\text{max}}^{\text{KBr}}$  6.17  $\mu$ ,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  266 m $\mu$  (log  $\epsilon$  4.36), 419 m $\mu$  (log  $\epsilon$  4.58), is assigned structure I<sup>5</sup> on the basis of the relationship of its spectral properties to those of II and other evidence given. Oxidation with potassium permanganate or ozone gave benzil and benzoic acid. Reduction with zinc and acetic acid at reflux yielded 1,2-diphenyl-1-propanone (III), 1,2-diphenyl-1-propene and  $\beta$ -1,2-diphenyl-1-propyl acetate; reduction with Raney nickel gave III and  $\beta$ -1,2-diphenyl-1-propanol. The carbonyl stretching band of I is abnormally weak, as is that of IV, yellow needles, m.p. 157.5–158°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  6.20  $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  257 m $\mu$  (log  $\epsilon$  4.03), 350 m $\mu$  (log  $\epsilon$  4.20); this effect is attributed to an *s-cis* conformation of the  $\alpha,\beta$ -unsaturated carbonyl systems. The remarkable stability of the desaurin system is attested by the failure of I to react with concentrated sulfuric acid or with zinc and acetic acid at room temperature, and its recovery (96%) on treatment with concentrated hydrochloric acid at reflux for 100 hours.

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(4) On a scale in which the aromatic toluene peak is assigned a value of 1000 c.p.s.; the spectrum was taken in chloroform solution with a Varian model V4300B spectrometer at 40 me. rf.

(5) This structure implies no distinction between the two possible geometrical isomers.