TPN^+ 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.[10,11] Incubation of 0.1 μmole of S^{35}-PAPS with the sulfate reducing system (Table I, $^1/_5$th scale) in the absence of ATP yielded 0.5 mμmole of $S^{35}O_2$ although 1.9 mμmoles was formed from an equivalent amount of $S^{35}O_4^{=}$ (0.1 μmole) and ATP (0.2 μmole). $S^{35}O_2$ was not formed from S^{35}-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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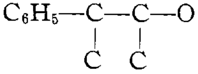
RECEIVED JULY 23, 1958

THE STRUCTURE OF THE DESAURINS

Sir:

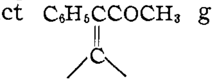
The desaurins form a class of stable, high-melting, neutral, yellow compounds obtainable most readily by the reaction of certain ketones with base and carbon disulfide; structure I was suggested for the prototype, the desaurin from deoxybenzoin.[1] Although this proposal subsequently was accepted,[2] 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°, $\lambda_{\max}^{CHCl_3}$ 6.05 μ, $\lambda_{\max}^{CHCl_3}$ 246 mμ (log ε 3.96), 374 mμ (log ε 4.44) (*Anal.* Calcd. for $C_{20}H_{16}O_2S_2$: 2 C–CH_3, 8.53; mol. wt., 352. Found: C–CH_3, 7.34; mol. wt., 355).[3] Reduction with zinc and base gave two equivalents of 3-phenyl-2-butanone, establishing the presence of two



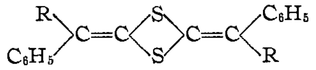
$C_6H_5\text{—}\underset{\underset{\textstyle C}{|}}{C}\text{—}\underset{\underset{\textstyle C}{|}}{C}\text{—}O$

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°, $\lambda_{\max}^{CHCl_3}$ 3.01, 6.05, 6.18, 6.27 μ, $\lambda_{\max}^{CHCl_3}$ 356 mμ (log ε 4.37), 450 mμ (log ε 4.36), a *bis*-2,4-dinitrophenylhydrazone, purple brown powder, m.p. 285–286°, $\lambda_{\max}^{KBr}$ 3.06, 6.19, 6.32 μ, $\lambda_{\max}^{CHCl_3}$ 260 mμ (log ε 4.26), 341 mμ (log ε 4.30), 505 mμ (log ε 4.34), and a dioxime, yellow needles, m.p. 209.5–210° dec., $\lambda_{\max}^{KBr}$ 3.00, 6.17 μ, $\lambda_{\max}^{EtOH}$ 250 mμ (shoulder, log ε 4.04), 267 mμ (shoulder, log ε 3.89), 347 mμ (log ε 4.31), 368 mμ (log ε 4.29); hydrolysis of the dioxime regenerated the desaurin, indicating the absence of gross structural change on derivativization. The desaurin gave a positive iodoform test and yielded with sodium hypochlorite an acid, $C_{18}H_{12}O_4S_2$, pale yellow microcrystals, m.p. 298–299° dec., $\lambda_{\max}^{KBr}$ 3.0–4.0, 6.02 μ, $\lambda_{\max}^{EtOH}$ 342 mμ (log ε 4.50), demonstrating that the carbonyl groups are present as two acetyl groups; this conclusion was corroborated by a strong band at 7.35 μ in the infrared and a single band at 1175 c.p.s.[4] 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

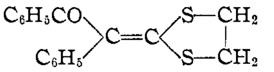


$C_6H_5\underset{\underset{\textstyle \diagup C \diagdown}{\|}}{C}COCH_3$

groupings and leads unambiguously to the structure II for the desaurin.[5]



I, R = COC_6H_5
II, R = $COCH_3$



IV

The desaurin from deoxybenzoin, golden needles, m.p. 300–302° dec, $\lambda_{\max}^{KBr}$ 6.17 μ, $\lambda_{\max}^{CHCl_3}$ 266 mμ (log ε 4.36), 419 mμ (log ε 4.58), is assigned structure I[5] 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 β-1,2-diphenyl-1-propyl acetate; reduction with Raney nickel gave III and β-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°, $\lambda_{\max}^{CHCl_3}$ 6.20 μ, $\lambda_{\max}^{EtOH}$ 257 mμ (log ε 4.03), 350 mμ (log ε 4.20); this effect is attributed to an *s-cis* conformation of the α,β-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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[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.

[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 mc. rf.

[5] This structure implies no distinction between the two possible geometrical isomers.