Carbon Disulfide. III. Reaction with Active Methylene Compounds. The Infrared and Ultraviolet Spectra of the Desaurins[1,2]

PETER YATES,[3] THOMAS R. LYNCH, AND DONALD R. MOORE
The Departments of Chemistry, University of Toronto, Toronto, Ontario, and Harvard University, Cambridge, Massachusetts 02138

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The position of the carbonyl-stretching bands in the i.r. spectra of the desaurins, 2,4-bis(acylmethylene)- and 2,4-bis(carboxymethylene)-1,3-dithetane derivatives, establishes that there is a strong interaction between the sulfur atoms and the carbonyl groups. This is considered to involve mainly conjugative interaction rather than interaction through space, although the latter may account for the abnormally weak intensity of the carbonyl-stretching bands. These bands are split in the case of several desaurins and related compounds, and evidence has been obtained in one case that the splitting is due to Fermi resonance. The u.v. spectra of the desaurins and related compounds also indicate a strong conjugative interaction between the sulfur atoms and the carbonyl groups.

La position des bandes de vibration des carbonyles dans les spectres i.r. des désaurines, des dérivés des bis(acylméthylène)-2,4 et bis(carboxyméthylène)-2,4 diéthane-1,3, démontre qu'il existe une interaction forte entre les atomes de soufre et les groupes carbonyles. Ces résultats proviendraient principalement d'une interaction conjugative plutôt que d'une interaction à travers l'espace, quoique cette dernière hypothèse pourrait expliquer l'intensité anormalement faible des bandes de vibration des carbonyles. Dans le cas de plusieurs désaurines et composés analogues, les bandes sont divisées et des indications ont été obtenues dans un cas, que cette division est due à de la résonance de Fermi. Les spectres ultraviolets des désaurines et des composés voisins indiquent aussi qu'une interaction conjugative forte existe entre les atomes de soufre et les groupes carbonyles.

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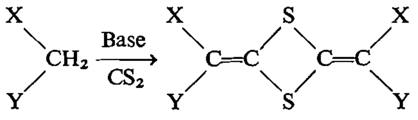
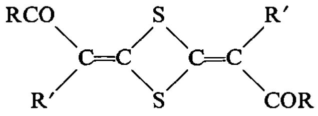
Preparation of Desaurins and Related Compounds

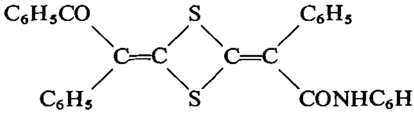
The desaurins, neutral compounds formed by the reaction of active methylene compounds **1** with base and carbon disulfide (eq. 1) have been shown to have structures of type **2**[4] (1, 3). We have described the preparation of the desaurins **3–7** previously (1). In studying the spectra of these desaurins, it was considered to be of importance to compare them with the spectra of a desaurin derived from a dialkyl ketone.

[1]


1 **2**



3 R = R′ = C_6H_5
4 R = CH_3; R′ = C_6H_5
5 R = OH; R′ = C_6H_5
6 R = C_6H_5; R′ = H
10 R = $(CH_3)_3C$; R′ = H



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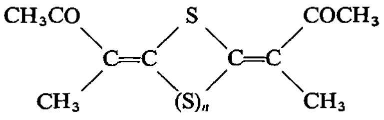

8 $n = 1$
9 $n = 2$

Previous to our investigation (3*b*), such a desaurin had not been prepared; however, during its course Kirby (4) reported the formation of the desaurin **8** by treatment of the trithiolane derivative **9** with triethyl phosphite. We pre-

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[1] For Paper II see ref. 1.

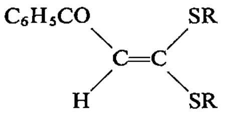
[2] The mass spectra of several desaurins have been discussed previously (2).

[3] Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Ontario.

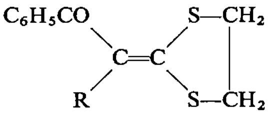
[4] In this and subsequent structures, no assignment of configuration is implied, except in the case of **6** (3).

pared the desaurin **10** by a modification of the general method of Gompper and Töpfl (5), whereby the dianion of the dithio acid formed by reaction of pinacolone with carbon disulfide and base was treated with oxalyl chloride.

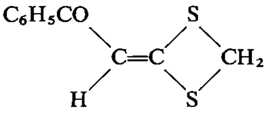
Four model compounds were also prepared for spectroscopic comparison with the desaurins. Compound **12** was first obtained by Kelber (6) by treatment of acetophenone with carbon disulfide and base to give benzoyldithioacetic acid (**11**), followed by methylation with methyl iodide and sodium; in the present work it was also prepared by methylation of **11** with methyl iodide and sodamide or with diazomethane. Its structure was confirmed by our spectroscopic observations and those of Gompper and Schaefer (7), and by an X-ray crystallographic study by Nyburg and Mellor (8).



11 R = H
12 R = CH_3



13 R = H
14 R = C_6H_5



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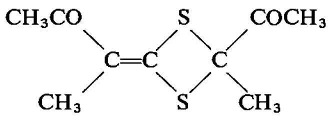


16

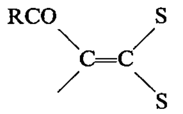
Compound **13** was prepared by the method of Kelber and Schwarz (9) by alkylation of **11** with 1,2-dibromoethane and base. These workers had established its structure by demonstrating that on reduction with zinc and sodium hydroxide it gave propiophenone and 1,2-ethanedithiol, thus establishing that both alkylations had occurred on sulfur.

Compound **14** was prepared by a similar alkylation with 1,2-dibromoethane of the salt of the β-keto dithio acid obtained from the action of carbon disulfide on the sodium derivative of deoxybenzoin. Its structure was established chemically by its reduction with zinc and sodium hydroxide to give *erythro*-1,2-diphenyl-1-propanol, isolated as its acetate (10), and 1,2-ethanedithiol, isolated as its dibenzoate (11). It has subsequently been confirmed by an X-ray crystallographic study by Schmidt and Tulinsky (12).

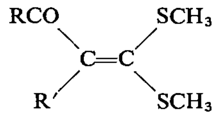
Compound **15** was prepared by alkylation of **11** with dibromomethane. Its structure is assigned on the basis of the close relationship of its i.r. and u.v. spectra (*vide infra*) to those of compounds **12** and **13**; its p.m.r. spectrum, with signals at δ 4.23 (s, 2H), 6.97 (s, 1H), 7.4–7.6 (m, 3H), and 7.8–8.0 (m, 2H), is in accord with this assignment. A related compound, **16**, has been obtained by Kirby (4) by the reaction of 3-diazo-2-butanone with carbon disulfide; its structure was established by an X-ray crystallographic study by Kapecki *et al.* (13).

Infrared Spectra of Desaurins and Related Compounds

Bands in the 2.8–3 and 5–6.5 μ regions of the i.r. spectra of the desaurins and of model compounds are listed in Tables 1 and 2, respectively. The spectra of the symmetrical desaurins **4**, **8**, and **10** with the group **17** show bands attributable to carbonyl-stretching vibrations at 6.05–6.07 μ. This position is at longer wavelength than that normally observed for simple α,β-unsaturated ketones, and indicates that the sulfur atoms interact with the carbonyl groups through the conjugated π-electron system and/or directly through space (*vide infra*).



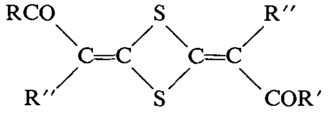
17 R = alkyl



18 R = alkyl; R′ = H
19 R = R′ = alkyl

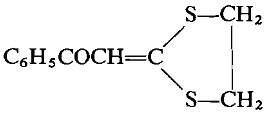
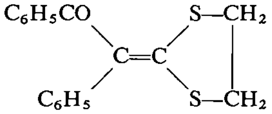
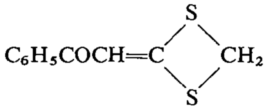
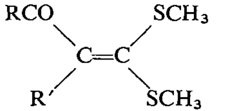
Thuillier and Vialle (14) have examined the spectra of a number of compounds of type **18** and **19**. The former type of compound was found to have its carbonyl-stretching band at *ca.* 6.10 μ, while the latter type showed this band at *ca.* 5.90 μ. The striking effect of the introduction of an alkyl substituent in place of hydrogen at the vinylic carbon atom adjacent to the carbonyl group is most readily interpreted as being the result of a change in the nature of the preferred conformation (15). In these terms, a planar or near-planar *s-cis* conformation, **23**, is assigned to the compounds of type **18** (the *s-trans* conformation, **24**, would involve steric crowding of the R group and one of the sulfur

TABLE 1. The i.r. spectra of the desaurins

	Compound 			Medium*	λ_{max} (μ)
	R = R'		R''		
3	C_6H_5		C_6H_5	K	6.17, 6.26(m), 6.36(m)
4	CH_3		C_6H_5	C	6.05, 6.24(m), 6.35(w)
5	OH		C_6H_5	K	3.0–4.0, 6.02, 6.25(w), 6.32(m)
6	C_6H_5		H	N	6.18, 6.26(m), 6.34(m)
8†	CH_3		CH_3	C	6.06
10	$(CH_3)_3C$		H	C	6.07, 6.15(sh)
20‡	$NHCH_3$		H	N	3.12, 6.10
21‡	NHC_2H_5		H	N	3.02, 6.14
22‡	$NHCH_2C_6H_5$		H	N	3.05, 6.10
	R	R'	R''		
7	C_6H_5	NHC_6H_5	C_6H_5	K	(*i*)§ 2.96(w), 6.02, 6.14, 6.25(m), 6.35(m) (*ii*)‖ 2.97(w), 6.03, 6.14, 6.27(m), 6.35(m)

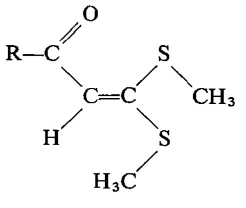
*K, potassium bromide or iodide disc; N, Nujol mull; C, chloroform solution.
†Reference 4.
‡Reference 16.
§Melting point 258–259°.
‖Melting point 210–211°.

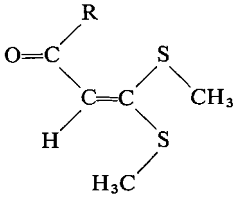
TABLE 2. The i.r. spectra of compounds related to the desaurins*

	Compound	Medium†	λ_{max} (μ)
12	$C_6H_5COCH{=}C(SCH_3)_2$	C	6.13, 6.18, 6.25(m), 6.34(m)
13		C	6.18, 6.25(m), 6.34(m)
14		C	6.20, 6.25, 6.35(m)
15		C	6.15, 6.21, 6.24(sh), 6.34(m)
18‡	$RCOCH{=}C(SCH_3)_2$ (R = alkyl)	K	6.09–6.10
19‡	 (R = R' = alkyl)	K or L	5.88–5.91

*For the spectra of additional related compounds, see refs. 5 and 17.
†C, chloroform solution; K, potassium bromide disc; L, liquid film.
‡Reference 14.

atoms). In compounds of type **19**, the analogous conformation, **25**, suffers from severe steric interaction between an S—CH_3 group and the R′ group, and probably also a further interaction between the R and R′ groups, due to a buttressing effect. As a result, compounds of type **19** are considered to take up a conformation in which there is a considerable departure from coplanarity, thus inhibiting the interaction of the carbonyl, ethylenic, and methylthio groups.


23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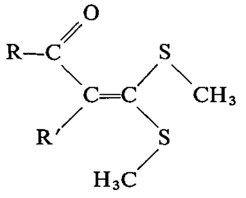
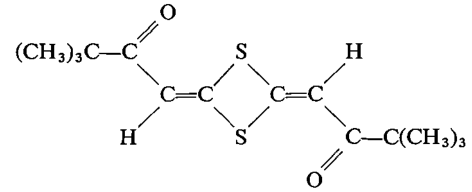
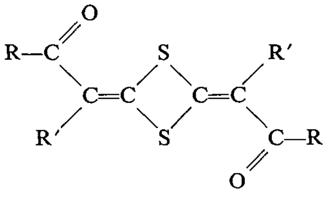
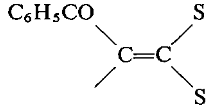

25

The desaurin **10** is expected to have the preferred conformation **26**, analogous to **23**, and this is reflected in the similarity of the position of its carbonyl-stretching band to that in the case of compounds of type **18**. The small shift to shorter wavelength may be due to the fact that in **23**, the two sulfur atoms interact through the conjugated system with a single carbonyl group, whereas in **26**, the two sulfur atoms interact with two carbonyl groups. The similarity of the carbonyl-stretching band positions for the desaurins **4**, **8**, and **10** suggests that **4** and **8** have preferred conformations of type **27**, analogous to **26**. In the case of **4**, this would require that the phenyl substituents (R′) be rotated considerably out of the plane of the conjugated carbonyl system.


26


27

The symmetrical desaurins **3** and **6** and the model compounds **12**–**15**, all having the grouping **28**, give rise to carbonyl-stretching bands at longer wavelengths than those of the compounds with the grouping **17**. A double *s-cis* conformation has been established for **6** in the solid state (3) and the shift of its carbonyl-stretching band relative to the desaurin **10**, which has been assigned this conformation also, is attributable to the additional conjugation of the carbonyl groups with the aromatic rings. The magnitude of the shift (*ca.* 0.10 μ) is similar to that found in cognate cases (18). The spectrum in the 6.1–6.4 μ region of the model compound **13** resembles that of **6**; however in the spectra of **12**[5] and **15** two bands of approximately equal intensity appear between 6.13 and 6.21 μ in addition to lower intensity bands at 6.25 and 6.34 μ, attributable to the phenyl rings. Thus it appears that in these compounds the carbonyl bands are split.[6] The origin of the splitting will be discussed subsequently; it may be noted here that if the unsplit band positions are approximated by the average of the positions of the split bands, the range of carbonyl-stretching absorption for the compounds with the grouping **28** is 6.15–6.20 μ.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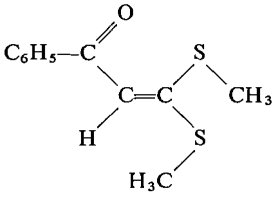
29

The positions of the carbonyl-stretching bands of the non-ketonic desaurins listed in Table 1 are readily related to those of the ketonic

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[5] This compound has been shown to have the *s-cis* conformation **29** in the solid state with a close approach of the α,β-unsaturated carbonyl system and the sulfur atoms to coplanarity (8).

[6] Ill-defined shoulders on the low wavelength sides of the bands at 6.18 and 6.20 μ of **13** and **14**, respectively, suggest that there may be some splitting in these cases also.

desaurins discussed already. The acid **5** has its carbonyl-stretching band at slightly shorter wavelength than the bands of **4**, **8**, and **10**, in conformity with the usual relationship between conjugated acids and conjugated ketones. Further, the amides **20**–**22** (16) have their carbonyl-stretching bands at slightly longer wavelength than the bands of **4**, **8**, and **10** in accord with the usual relationship between conjugated ketones and conjugated amides.

It has previously been reported (19) that the carbonyl-stretching bands of the desaurin **8** and the model compound **14** are abnormally weak; this conclusion was based on a qualitative examination of the spectra. Quantitative measurements have confirmed this in the case of **3**. The integrated intensity[7] of its 6.17 μ band measured in potassium bromide discs,[8] was 1.71, corresponding to 0.86 per carbonyl group, while the integrated intensity of the carbonyl-stretching band of benzophenone, measured in potassium bromide discs under the same conditions, was 1.20. However, similar measurements on the desaurin **6** gave a value of 2.86, or 1.43 per carbonyl group. The sum of the integrated intensities of the bands at 6.13 and 6.18 μ of **12** in solution in chloroform was determined to be 1.39. This value is low in comparison with values reported in chloroform solution for dialkyl ketones and benzophenone, *i.e.*, 1.9 and 2.4[9] (22), respectively.[10] In the case of planar chromophores, conjugation with an ethylenic double bond or aromatic ring brings about an increase in the carbonyl-stretching band intensity (20, 22). While the positions of the carbonyl-stretching bands of **3**, **6**, and **12** show a considerably higher degree of conjugation than that in benzophenone, their intensities per carbonyl group are similar to, or less than, that of the carbonyl-stretching band of benzophenone. This suggests that there is a significant reduction in intensity relative to simple conjugated ketones associated with the grouping **28** present in these compounds. The intensity relationships among **3**, **6**, and **12** may well reflect differences in the extent of coplanarity between the phenyl rings of the benzoyl groups and the α,β-unsaturated carbonyl system.[11]

The abnormally long wavelength of the carbonyl-stretching bands of the desaurins and related compounds and the reduced intensity of these bands raises the question whether these effects are due to an interaction through space between the sulfur and oxygen atoms in the *s-cis* conformations of these compounds. Recent X-ray crystallographic data have made it clear that for several of these compounds in the solid state the S—O distance is considerably shorter than the sum of the van der Waals' radii of sulfur and oxygen (3.05 Å),[12] *i.e.*, **6** (2.64 Å) (3, 8), **12** (2.72 Å) (8), **14** (2.70 Å) (12), and **16** (2.63 Å) (13).[13] However, 3-methylthio-2-cyclohexenone (**30**), which perforce has an *s-trans* relationship between the sulfur atom and the carbonyl group, gives rise to a carbonyl-stretching band in its neat or solution i.r. spectrum at 5.98–6.01 μ (26). This suggests that the effect of direct sulfur–oxygen interaction on the wavelength of the carbonyl-stretching vibrations in the desaurins and related compounds is relatively small, since compounds of type **18** absorb at 6.09–6.10 μ and the bathochromic shift of 0.10 μ is attributable in major part to increased conjugation resulting from the presence of the second sulfur atom.[14] Such an interaction may contribute significantly, however, to the reduction of band intensities, since the integrated intensity reported for **30** in solution is 2.70 (26), which is comparable or larger in magnitude than the values measured or estimated for the much

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[7] Integrated absorption intensities are given in absorbance units (20): 1 absorbance unit = 1 × 10^4 mol^{-1} l cm^{-2}.

[8] Although integrated intensities are not normally measured in potassium bromide discs, this medium has been used with success for the analysis of mixtures (21*a*), and Lambert's and Beer's laws have been shown to hold (21).

[9] This was measured in the present work also and found to be 2.35.

[10] It has previously been found that absorptivities are greater in solution than in the solid state (23).

[11] The planes of these phenyl rings in **6** and **12** in the solid state have been shown to be inclined at 10 and 19°, respectively, to the planes of the α,β-unsaturated carbonyl systems (8). The angle is expected to be significantly larger in the case of **3** (*cf.* 12). It may be noted that benzophenone is itself nonplanar (24).

[12] This figure is based on a van der Waal's radius for sulfur of 1.65 Å (3*b*, 8), derived from the S—S contact distances in rhombic sulfur (25).

[13] For interpretations of these short S—O distances in terms of partial bonding between sulfur and oxygen, see refs. 3*b* and 8.

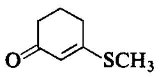
[14] Mollier *et al.* (27) have concluded that partial sulfur–oxygen bonding in the related case of 1,2-dithiol-3-ylidene ketones brings about a large shift of the carbonyl-stretching band to longer wavelength. However, Kapecki and Baldwin (28) have concluded from extended Hückel molecular orbital calculations that covalent bonding between sulfur and oxygen is negligibly weak in related cases.

TABLE 3. The u.v. spectra of the desaurins and related compounds

Compound*	Solvent†	λ_{max} (mμ) (ε)
3	C	266(22 900), 419(38 100)
4	C	246(9120), 374(27 500)
5	E	342(31 600)
6	C	274(17 000), 377(sh, 45 700), 392(49 000)
8	E	241(sh, 1440), 359(28 700), 370(28 700)
10	E	242(2510), 350(29 500)
20	E′	293(sh), 305(35 500), 322(30 420)
21	E′	293(sh), 306(36 600), 325(30 950)
22	E′	295(sh), 309, 325
7	C	(*i*) 263(18 200), 401(37 200)
	C	(*ii*) 265(18 600), 387(39 800)
12	E	263(8710), 280(8710), 344(20 400)
13	E	258(7940), 287(6030), 344(20 900)
14	E	257(10 700), 350(15 800)
15	E	257(14 500), 344(22 900)
16	E	243(5360), 317(8950)

*See Tables 1 and 2 for structures of compounds and references.
†C, chloroform; E, 95% ethanol; E′, 90% ethanol.

more highly conjugated ketones **3**, **6**, and **12** in solution. Further investigation is necessary to establish this, since the carbonyl-stretching band intensities are often weaker for *s-cis* than for *s-trans* α,β-unsaturated ketones in the absence of any special interactions of the oxygen atom (15*a*).



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As has been noted earlier, several compounds with the grouping **28** have split carbonyl bands. A preliminary examination of the origin of the splitting was made in the case of compound **12**. In carbon tetrachloride solution the bands of equal intensity at 6.13 and 6.18 μ in chloroform solution were replaced by a sharp, intense band at 6.11 μ and a weak band at 6.18 μ. Such behavior could be due either to vibrational coupling or rotational isomerism (29). However, the latter origin is contra-indicated by the spectrum of **12** in a potassium bromide disc, which showed a sharp band at 6.20 μ with a medium intensity shoulder at 6.15 μ, and in a Nujol mull, which showed a broad band at 6.22 μ with a shoulder of medium intensity at 6.17 μ. Furthermore, the n.m.r. spectrum of **12** showed no temperature dependence in the range 27 to −60°. Thus the most probable sources of the bifurcation is vibrational coupling. Corroboration was sought by the preparation of **31**, *i.e.*, **12** with the vinylic hydrogen replaced by deuterium; n.m.r. spectroscopy indicated that there was *ca.* 70% incorporation of deuterium in the vinylic position.[15] In chloroform solution the i.r. spectrum of the labelled compound exhibited strong bands at 6.15 and 6.18 μ with a shoulder at 6.13 μ; in carbon tetrachloride the spectrum showed a strong, sharp band at 6.13 μ; in both spectra a band at 6.25 μ was also present. These observations are in accord with the attribution of the splitting of the carbonyl band of **12** to vibrational coupling, which is absent in the deuterated derivative **31**; the unperturbed carbonyl-stretching band positions are then 6.15 ($CHCl_3$) and 6.13 μ (CCl_4). This coupling could be with the fundamental stretching vibration of the ethylenic double bond or with an overtone or combination vibration (*i.e.*, Fermi resonance). If coupling to a fundamental vibration is involved, the estimates of the carbonyl-stretching band intensities made earlier may be too high, since they will also include the intensity of the other fundamental band; however, if Fermi resonance is involved, this error is unlikely to be significant because of the low intensity of overtone and combination bands. The data available do not permit a definitive choice between the two types of coupling, but the latter appears more probable. Jensen and Henriksen (17) have assigned a very intense band in the 6.5–7.0 μ region of the spectra of a series of compounds containing the function **32** to the ν_1 vibration of this grouping; they favored this assignment over one to a simple ethylenic stretching vibration because of the unusual intensity and long wavelength of the

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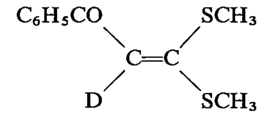
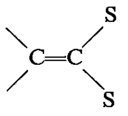
[15] We thank Mr. A. Hepworth for the preparation of the labelled compound and obtaining the related spectra.

bands. In the spectra of all of the desaurins and related compounds that we have examined, a strong or very strong band appears in the 6.5–6.9 μ region, which is probably analogous to the bands in this region observed by Jensen and Henriksen. If this is the case, the splitting of the carbonyl-stretching bands cannot involve coupling with an ethylenic stretching vibration and must have their origin in Fermi resonance.[16] Again, further work is needed to establish this unequivocally, since strong bands due to aromatic C—C stretching and aliphatic C—H bending vibrations can also occur in the 6.5–6.9 μ region.



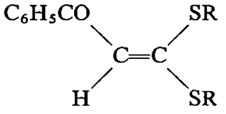
31



32

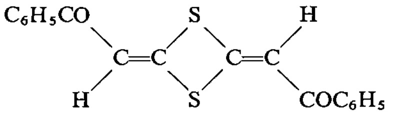
Ultraviolet Spectra of Desaurins and Related Compounds

The u.v. maxima of the desaurins and related compounds are listed in Table 3. The spectra of compounds **12**, **13**, and **15** with the grouping **33** have a high intensity, long wavelength maximum[17] at 344 mμ (ε 20 400 - 22 900) and another maximum at 257–263 mμ (ε 7940 -14 500).



33

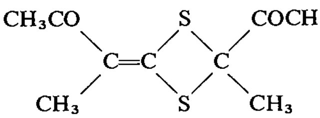
R = CH_3 or $(CH_2)_n$



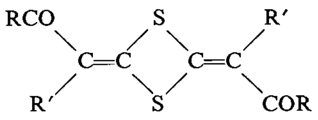
6

Introduction of a phenyl group in place of the vinylic hydrogen atom, as in **14**, causes a bathochromic and hypochromic shift of the long wavelength maximum to 350 mμ (ε 15 800), most probably due to extension of the chromophoric system with reduction in coplanarity (*vide supra*). The desaurin that is most closely related to compounds **12**, **13**, and **15** is **6**; its long wavelength maximum shows a bathochromic and hyperchromic shift with respect to the corresponding maxima of these compounds. The bathochromic shift is *ca.* 50 mμ and the hyperchromic shift > 1500 per carbonyl group. The spectrum of the desaurin **3** in which the vinylic hydrogen atoms of **6** are replaced by phenyl groups bears a similar relationship to that of **14**, showing a bathochromic shift of the long wavelength maximum of 69 mμ and a hyperchromic shift of *ca.* 3000 per carbonyl group. These shifts are consistent with transmission of delocalization through the sulfur atoms in the desaurins (4, 16). The suggestion (16) that such effects may be due in part to the unusual short S–S distance in the desaurins and the resulting enhanced transannular S–S overlap must be viewed with some reserve on the basis of the present data. In compound **15** it may be anticipated that the S–S distance will be very short and similar to that in **6** rather than that in **12** or **13**.[18] Yet, although the long wavelength maximum of **15** shows a hyperchromic shift with respect to the maxima of **12** and **13**, it shows no bathochromic shift whatsoever and differs markedly from **6** in this regard.

As would be anticipated, the long wavelength maximum of **16** occurs at appreciably lower wavelength than those of the phenyl ketones **12**, **13**, and **15** ($\Delta\lambda \sim -25$ mμ); its intensity is



16



8 R = R′ = CH_3
10 R = $C(CH_3)_3$; R′ = H
4 R = CH_3; R′ = Ph

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[16] Jensen and Henriksen (17) have also observed splitting of the carbonyl bands of certain of the compounds they have examined that have the ethylenic double bond of the grouping **32** conjugated with carbonyl groups. However, each of these has two such carbonyl groups, and the splitting may be due here to vibrational coupling between the carbonyl groups.

[17] These maxima are broad and unsymmetrical and may well represent the near superimposition of two peaks, as is suggested by the fact that some other compounds in Table 3 show either a high intensity shoulder on the long wavelength maximum or two close-lying long wavelength maxima of similar intensity; in the latter cases comparison is made with the average position of the maxima.

[18] *Cf.* the S–S distance in **16** (2.71 Å) (13) with that in **6** (2.67 Å) (3, 8), **12** (2.94 Å) (8), and **14** (2.95 Å) (12).

considerably lower also. The related desaurin **8** shows bathochromic and hyperchromic shifts analogous to those encountered in the phenyl ketone series ($\Delta\lambda \sim 50$ mμ; $\Delta\varepsilon \sim 5000$ per carbonyl group). The desaurin **10** that has no alkyl substituents on the ethylenic double bonds shows a shift of its longer wavelength maximum relative to that of **8** to lower wavelength ($\Delta\lambda \sim -15$ mμ), as expected. Conversely, substitution of phenyl for alkyl substituents on the ethylenic double bonds of **8** as in **4** leads to a bathochromic shift ($\Delta\lambda \sim 10$ mμ); the relatively small effect may be attributed to the deviation from coplanarity.

The non-ketonic desaurin spectra listed in Table 3 are readily related to those of the ketonic desaurins discussed above. The high intensity, long wavelength maximum of **5** occurs at shorter wavelength than that of the analogous ketone **4** ($\Delta\lambda \sim -30$ mμ; *cf.* benzoic acid *vs.* acetophenone: $\Delta\lambda \sim -15$ mμ). The amides **20**–**22** also give maxima at shorter wavelength than the maximum of the analogous ketone **10** ($\Delta\lambda \sim -35$ mμ; *cf.* benzamide *vs.* acetophenone: $\Delta\lambda \sim -20$ mμ). The spectra of the keto amides **7** are clearly also closely related to the spectrum of the diketone **3**.

Experimental

Melting points were taken on a Fisher–Johns micro hot stage and are uncorrected. Solutions in organic solvents were dried over anhydrous sodium sulfate.

The Desaurin from Pinacolone (10)

Pinacolone (20.0 g, 0.200 mol) was added dropwise to a cooled, stirred suspension of sodamide (8.00 g, 0.2005 mol) in anhydrous ether. When anion formation was complete, carbon disulfide (6.0 ml, 0.100 mol) was added slowly, and the yellow suspension formed was stirred for a further 5 min. Methanol (*ca.* 50 ml) was added to dissolve the suspension, and oxalyl chloride (10.0 ml, 0.120 mol) was added with great caution. The solution was stirred for a further 0.5 h, then transferred to a separatory funnel, and water and benzene were added. The organic layer was separated and washed several times with aqueous 10% sodium hydroxide, once with water, and dried. After removal of the solvent, hexane was added to the residue, and the precipitate (1.0 g) was filtered off. Crystallization of the solid from chloroform–hexane gave **10** (0.50 g, 4%), m.p. *ca.* 258°. Four further recrystallizations from chloroform–hexane gave an analytical sample, m.p. 259.5–260° (corrected).

Anal. Calcd. for $C_{14}H_{20}O_2S_2$: C, 59.11; H, 7.09; S, 22.55. Found: C, 59.00; H, 7.09; S, 22.62.

Benzoyldithioacetic Acid (11)

Acetophenone (120.6 g, 1.00 mol) was added dropwise to a stirred suspension of commercial sodamide (39.0 g, 1.00 mol) in benzene (250 ml) at room temperature under nitrogen. When the brisk evolution of ammonia was nearly complete, the sodium derivative of acetophenone separated suddenly to form a thick off-white paste. Additional benzene (100 ml) was added to facilitate stirring, which was continued while the system was swept with nitrogen until the evolution of ammonia appeared to be complete (negative test with moist litmus paper).

Carbon disulfide (100 g, 1.31 mol) was added under a current of nitrogen, and the deep orange suspension was stirred for 1 h. The slurry was poured onto ice (300 g), and the mixture was stirred thoroughly; the benzene layer was separated and washed with three portions of aqueous 10% sodium hydroxide. The combined basic extracts and original aqueous layer were cooled to 5° and neutralized with ice-cold 10% sulfuric acid while the temperature was maintained below 10°. At the neutral point a red-brown mass separated, accompanied by a vigorous evolution of hydrogen sulfide. Excess acid was added, and the mixture was filtered. The crude solid acid was washed with ice-cold water and air-dried at room temperature. The yield of crude benzoyldithioacetic acid was 90 g (46%).

Two recrystallizations of the crude acid from petroleum ether (b.p. 30–60°) gave golden leaflets, m.p. 62–64°, satisfactory for further reactions. Two further recrystallizations afforded a sample, m.p. 62.5–64° [lit. (30) m.p. 63–64°]; $\lambda_{max}(CHCl_3)$ 3.9–4.2 (w), 6.25 (m), 6.29 (ms), 6.45 μ (s); $\lambda_{max}(C_2H_5OH)$ 231 (ε 9300), 266 (ε 7800), 355 mμ (ε 14 800).

Methylation of 11. Preparation of 12

(A) Benzoyldithioacetic acid (**11**; 2.00 g, 10.2 mmol) was methylated by treatment with sodium and methyl iodide by the method of Kelber (6). Two recrystallizations of the product from ethyl acetate – ligroin (b.p. 66–75°) gave **12** as bright yellow needles (0.80 g, 35%), m.p. 93.5–94.0°, [lit. (6) m.p. 93–94°]; $\delta(CDCl_3)$ 2.52 (s, 3H), 2.54 (s, 3H), 6.73 (s, 1H), 7.42 (m, 3H), 7.86 (m, 2H); the n.m.r. spectrum was unchanged when recorded at −60°.

(B) A solution of **11** (1.00 g, 5.1 mmol) in ether (25 ml) was treated with 0.6 *N* ethereal diazomethane (20 ml). The mixture was allowed to stand at room temperature for 3 days. The ether was then removed on the steam bath, and the residue was chromatographed on alumina (Merck; 75 g). A small amount of yellow oil (0.035 g) was eluted with 50% petroleum ether in benzene. The major yellow band was eluted with dichloromethane to give **12** (0.85 g, 74%). After crystallization from ethyl acetate – ligroin this had m.p. 93.0–93.5°, undepressed on admixture with the product obtained by the procedure of Kelber (6).

Alkylation of 11 with 1,2-Dibromoethane. Preparation of 13

Benzoyldithioacetic acid (**11**; 10.00 g, 51.0 mmol) was alkylated with 1,2-dibromoethane by the method of Kelber and Schwarz (9) to give **13** (6.0 g, 53%). Two recrystallizations from ligroin (b.p. 66–75°) afforded bright yellow needles, m.p. 83–83.5° [lit. (9) m.p. *ca.* 80°].

Alkylation of 11 with Dibromomethane. Preparation of 15

Benzoyldithioacetic acid (**11**; 5.00 g, 25.5 mmol) was dissolved in water (100 ml) containing potassium hydroxide (6.00 g, 107 mmol). Dibromomethane (8.00 g, 59.7 mmol) was added, and the mixture was stirred at room temperature for 12 h and then extracted with four portions of dichloromethane. The combined extracts were dried, filtered, and stripped of the bulk of the dichloromethane on the steam bath. The crude product was dissolved in benzene (25 ml), and the solution was boiled briefly to expel dichloromethane, cooled, and chromatographed on alumina (Merck; 150 g). The major fraction was eluted immediately with benzene to give **15** as stout yellow needles (2.0 g, 38%). Three recrystallizations from cyclohexane afforded fine, pale cream needles, m.p. 128–129°.

Anal. Calcd. for $C_{10}H_8OS_2$ (mol. wt 208): C, 57.66; H, 3.97; S, 30.79. Found (241 (Rast)): C, 57.50; H, 3.73; S, 30.54.

Preparation of 14

Deoxybenzoin (10.00 g, 50.9 mmol) was dissolved in benzene (300 ml), sodamide (2.0 g, 51.2 mmol) was added, and the mixture was boiled under reflux under nitrogen with stirring for 12 h. The sodium derivative of deoxybenzoin separated as a pale yellow suspension, and ammonia could no longer be detected in the effluent (moist litmus paper test). The stirred suspension was cooled and carbon disulfide (4.00 g, 51.3 mmol) was added. Stirring was continued for 5 days at room temperature; the suspension gradually assumed an orange-red color.

One-half of this reaction mixture was treated with 1,2-dibromoethane (4.80 g, 25.6 mmol), and the resulting mixture was boiled under reflux under nitrogen with stirring for 2 days. The mixture was filtered, and the solvent was removed from the filtrate under reduced pressure to give an orange solid (3.53 g). This was dissolved in benzene and chromatographed on alumina (Merck; 100 g). The column was thoroughly eluted with benzene, to give a yellow semi-solid product (1.70 g), whose i.r. spectrum indicated it to be largely deoxybenzoin. Elution of the column with chloroform gave **14** as a yellow-orange solid (1.40 g, 18%). This was recrystallized four times from aqueous ethanol to give small yellow needles, m.p. 157.5–158°.

Anal. Calcd. for $C_{17}H_{14}OS_2$: C, 68.42; H, 4.73; S, 21.49. Found: C, 68.42; H, 4.79; S, 21.69.

Reduction of 14 with Zinc and Base

A mixture of **14** (0.100 g, 0.335 mmol), sodium hydroxide (1.00 g, 25 mmol), zinc dust (1.00 g, 15.3 mg-atoms), ethanol (10 ml), and water (20 ml) was boiled under reflux. After 2 days additional sodium hydroxide (1.00 g, 25 mmol) and zinc dust (0.50 g, 7.6 mmol) were added. After 5 days the solution was cooled, filtered, and extracted with dichloromethane. The extract was dried, filtered, and stripped of solvent on the steam bath to give a pale yellow oil (0.058 g), whose i.r. spectrum showed it to be largely *erythro*-1,2-diphenyl-1-propanol. This was treated with pyridine (2.0 ml) and acetic anhydride (1.0 ml), and the mixture was heated for 4 h on the steam bath. The solution was poured into water, acidified to p*H* 1 with 10% hydrochloric acid, and extracted with dichloromethane. The extract was dried, filtered, and evaporated to give a crystalline mass (0.038 g), which was recrystallized from ethanol to give fine, colorless cubes, m.p. 107–108.5°, undepressed on admixture with *erythro*-1,2-diphenyl-1-propyl acetate (1, 10). The i.r. spectra of the two samples were identical.

The aqueous basic layer from the original extraction was diluted to 75 ml with water and evaporated nearly to dryness under reduced pressure. Water (50 ml) and benzoyl chloride (2.0 ml) were added. The mixture was shaken until no further warming was apparent and then filtered. The white precipitate (0.032 g) was recrystallized from ethanol–water to give colorless prisms, m.p. 92–92.5°, undepressed upon admixture with 1,2-ethanedithiol dibenzoate [lit. (11) m.p. 94.5–95°]. The i.r. spectra of the two samples were identical.

The yields of *erythro*-1,2-diphenyl-1-propyl acetate and 1,2-ethanedithiol dibenzoate were 45 and 31%, respectively.

Preparation of 31

A solution of acetophenone (2.50 g, 20.8 mmol) in dioxane (40 ml) containing deuterium oxide (18 ml, 1.00 mol) and a catalytic quantity of anhydrous potassium carbonate was boiled under reflux for 1 h. When cool, the solution was extracted with ether, and the dioxane was removed from the ethereal solution by washing with water. The acetophenone obtained after removal of the solvent showed 75% exchange of the α-hydrogen atoms by n.m.r. spectroscopy. The treatment was repeated using sodium-dried dioxane, and the product was distilled to give acetophenone-2-d_3 with 92% of the α-hydrogen atoms replaced by deuterium.

Acetophenone-2-d_3 (0.120 g, 1.00 mmol) was added to a suspension of sodamide (0.030 g, 1.00 mol) in anhydrous benzene. When anion formation was complete, carbon disulfide was added in excess, and after 15 min the excess carbon disulfide was boiled off. Sodamide (0.039 g, 1.00 mmol) was added, followed by methyl iodide (0.280 g, 2.00 mmol), and the reaction mixture was stirred overnight. Water was added, and the organic layer was separated, dried, and stripped of solvent. Addition of hexane to the residue caused it to crystallize, and filtration gave crude **31** (0.040 g, 18%). Recrystallization of the crude material from ethyl acetate – pentane gave **31**, m.p. 92.5–93.5° (corrected), undepressed on admixture with **12**. The ratio of the intensity of the vinylic proton signal at δ 6.73 to the intensities of the methyl proton signals at δ 2.52 and 2.54 in the n.m.r. spectrum of **31** showed *ca.* 70% incorporation of deuterium at the vinylic position.

Infrared Spectral Intensity Measurements

The spectra were recorded with a Perkin–Elmer 521 Grating Infrared Spectrophotometer [linear in frequency (ν)], whose horizontal scale was expanded by a factor of 4. Absorption bands, measured by the machine as percent transmittance, were replotted on the absorbance (A) scale, and integrations were performed by the method of cutting out and weighing. The solution spectra were obtained in chloroform solution with the use of two 0.5 mm cells, with Teflon spacers; the path length of the sample cell was determined to be 0.501 mm by the method of Sutherland and Willis (31). Potassium bromide pellets were made by adding a weighed sample of the compound to *ca.* 250 mg of anhydrous potassium bromide (Harshaw) in a "Wig-L-Bug"; the mixture was then ground for 3 min, and all pellets were pressed for identical times and at identical pressures; a blank pellet was placed in the reference beam.

The integrated intensities, B (mol l^{-1} cm^{-2}), for the solution spectra were obtained by the use of the formula:

$$B = \frac{1}{cl}\int A\,\mathrm{d}\nu,$$

where c is the concentration in mol l^{-1} and l is the path length in cm. For the pellet spectra, since c = mol/(area of pellet × l), the formula becomes:

$$B = \frac{\text{area of pellet}}{\text{mol}}\int A\,\mathrm{d}\nu$$

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