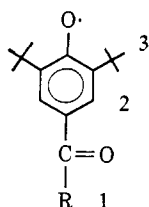


Table III. ESR Coupling Constant of



Compound	Position	a , oersteds
R = H	1	0.4
	2	2.2
	3	0.08
R = CH ₃	1	0.28
	2	2.2
	3	0.09
R = <i>t</i> -butyl	1	0.17(?)
	2	2.2
	3	0.09
R = phenyl	1	Small
	2	2.2
	3	0.08

coupling constants of the two different types of *t*-butyl protons in radical IIc, because of the large number of overlapping lines and the relatively poor resolution of the esr spectrum. It appears, however, that the splitting from the *t*-butyl group attached to the carbonyl has about twice the coupling constant of the *t*-butyl groups on the aromatic ring. No splitting was observed from the unsubstituted phenyl group in either radical Id or IId. Coupling constants for the phenoxy ketones are given in Table III.

Radicals IIa-d dimerize in solution and exist entirely as dimers in the solid state.¹⁴ Radicals Ia-c appeared to be entirely monomeric in solution. These radicals had a normal Curie temperature dependence as far as we could tell. The dimerization of the phenoxy ketones made it impossible to determine the molar extinction coefficients of the optical transitions.

Conclusion

The change in the nitrogen coupling constants of radicals Ia-d appears to be due to changes in the angle between the plane of the phenoxy aromatic ring and the plane formed by the RC=N group. As the steric bulk of the R group increases, this angle becomes larger and the nitrogen coupling constant decreases. This variation in twist angle is also reflected in the decrease of the molar extinction coefficients of the optical spectra, with an increase of steric bulk of the R groups. The nmr and ultraviolet spectra of the phenols, from which these radicals were made, indicate that these compounds also exist with different twist angles.

The small splittings from the CHO and O=CCH₃ protons in radicals IIa and b might be explained by twisted conformations. Protons in the same positions on compounds Ia and b have coupling constants about a factor of five larger. Although other factors may determine the relative magnitudes of the coupling constants of the R groups, a possible explanation is a large difference in twist angles.

Acknowledgments. This work was supported in part by National Science Foundation Grant GP-5482. The author wishes to thank Mr. M. Sakamoto for assistance in the calculations of the theoretical spectra.

(14) We shall discuss the structures of the dimers and the radical-dimer equilibria in a later publication.

Solvent Effects in Nuclear Magnetic Resonance Spectroscopy. IX.¹ A Variable-Temperature Study of α,β -Unsaturated Ketones in Toluene-*d*₈ Solution

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Contribution from the University Chemical Laboratory, Cambridge, England.
Received July 5, 1966

Abstract: A variable-temperature proton magnetic resonance study of a series of α,β -unsaturated ketones (fixed *s-trans* and *s-cis* systems, as well as mobile systems) has been made in toluene-*d*₈ solution. Stereospecific complexing between the α,β -unsaturated ketones and the toluene-*d*₈ solvent results in temperature-dependent chemical shifts of the proton resonances. The direction of change of the temperature-dependent chemical shift (upfield or downfield) is dependent on the location of the proton with reference to a plane drawn through the carbonyl carbon atom and perpendicular to the C-O bond. This generalization may be utilized in both structural and conformational studies of α,β -unsaturated ketones.

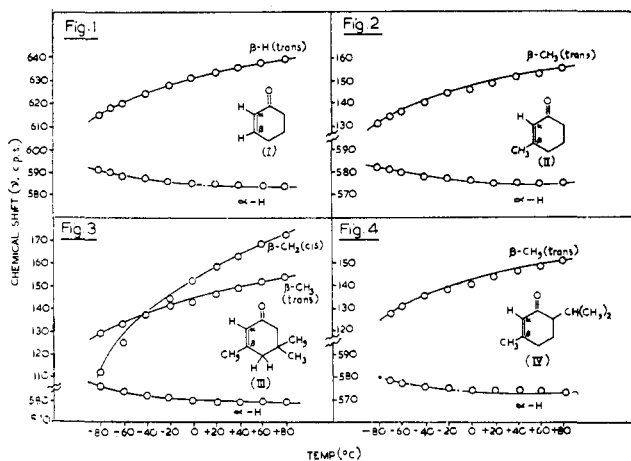
Recently it has been shown^{2,3} that the solvent shifts ($\Delta = \delta_{\text{CDCl}_3} - \delta_{\text{C}_6\text{H}_6}$, ppm) induced by benzene (relative to deuteriochloroform) in the proton magnetic

resonance spectra of saturated ketones are positive for protons lying behind a reference plane drawn through the carbonyl carbon atom and perpendicular

(1) Part VIII: J. H. Bowie, J. Ronayne, and D. H. Williams, *J. Chem. Soc., Sect. B*, 785 (1966).

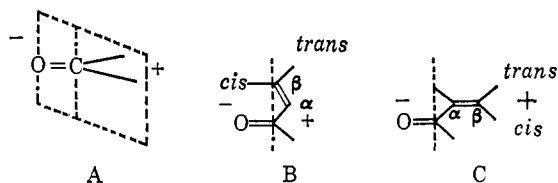
(2) J. D. Connolly and R. McCrindle, *Chem. Ind. (London)*, 375 (1965).

(3) D. H. Williams and N. S. Bhacca, *Tetrahedron*, 21, 2021 (1965).



Figures 1-4. Temperature variation of the chemical shift (cps at 100 Mc) of some proton resonances of cyclohex-2-en-1-one (I), 3-methylcyclohex-2-en-1-one (II), isophorone (III), and piperitone (IV), respectively.

to the C-O bond. Protons in front of the reference plane have a negative Δ value, while those lying in or near the plane have small or zero Δ values. This generalization, which is summarized diagrammatically in A, also appears to hold for α,β -unsaturated ketones.^{4,5} In the light of the relatively small solvent shifts which are induced on passing from dilute deuteriochloroform solution to a dilute carbon tetrachloride solution,⁶ the generalization for α,β -unsaturated ketones appears applicable if either carbon tetrachloride⁵ or deuteriochloroform⁴ is employed as reference solvent (i.e., $\Delta = \delta_{\text{CCl}_4} - \delta_{\text{C}_6\text{H}_6}$ or $\Delta = \delta_{\text{CDCl}_3} - \delta_{\text{C}_6\text{H}_6}$ ppm).



The selective shifts in ketones are consistent with an interaction between the solute carbonyl compound and the solvent benzene. An approximate, thermally averaged, spatial arrangement between solvent and solute molecules which can account for the observed shifts in sign and magnitude has been indicated for 5 α -androst-11-one.⁷ Such an approach is only justified in terms of the desirability to indicate pictorially for a suitable case the stereospecificity which would be necessary to account for the empirical law, and it is emphasized that the physical basis for the picture is crude. The supplementary shifts which are observed on cooling solutions of ketones in toluene-*d*₈ are roughly proportional to the Δ values, and on the basis of a predominant 1:1 complex (which is consistent with dilution experiments), approximate thermodynamic parameters for the weak interaction may be calculated.⁸ The chemical shifts in toluene-*d*₈ solution are temperature variable because on lowering the temperature the

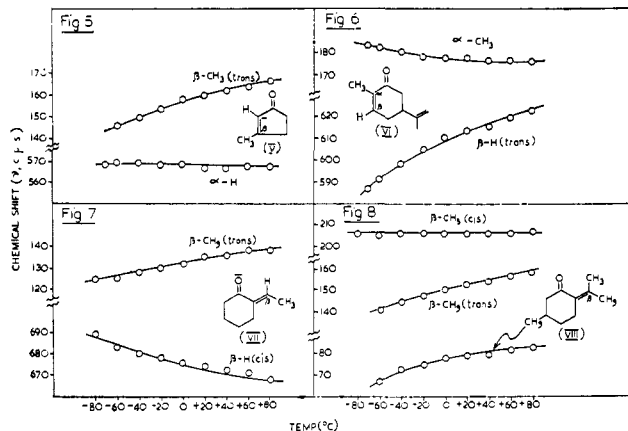
(4) D. H. Williams, *Tetrahedron Letters*, 2305 (1965).

(5) C. J. Timmons, *Chem. Commun.*, 576 (1965).

(6) P. Laszlo, *Bull. Soc. Chim. France*, 85 (1964).

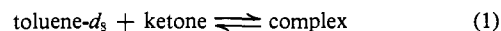
(7) D. H. Williams and D. A. Wilson, *J. Chem. Soc., Sect. B*, 144 (1966).

(8) P. Laszlo and D. H. Williams, *J. Am. Chem. Soc.*, **88**, 2799 (1966); see also R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **44**, 37 (1966).

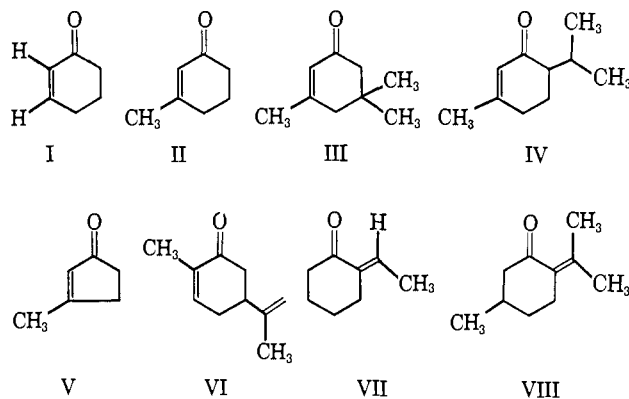


Figures 5-8. Temperature variation of the chemical shift (cps at 100 Mc) of some proton resonances of 3-methylcyclopent-2-en-1-one (V), carvone (VI), *trans*-2-ethylidenecyclohexanone (VII), and pulegone (VIII), respectively.

equilibrium (1) is displaced towards complex formation.



The purpose of the present work was to determine the proton magnetic resonance spectra of a number of fixed *s-cis* (see B) and *s-trans* (see C) α,β -unsaturated ketones over a range of temperatures in toluene-*d*₈, to determine whether the signs of the shifts produced on cooling followed the empirical law (see A, B, C). If this proved to be the case, then the variable-temperature curves of the various protons in labile α,β -unsaturated ketones could be used to indicate the predominance of *s-cis* or *s-trans* forms. Some Δ values (as opposed to variable-temperature shifts) for labile α,β -unsaturated ketones have recently been utilized in a similar manner.⁵



The results which have been obtained for the fixed *s-trans* (I-VI) and *s-cis* (VII and VIII) compounds will be considered first and are summarized in Figures 1-8. These figures give plots of the chemical shifts (cps at 100 Mc) of proton resonances of the ketones against temperature in a dilute toluene-*d*₈ solution. All compounds were studied in the temperature range +80 to -60, -70, or -80°. The nomenclature which will be used to define the location of a substituent (proton or methyl) on the enone chromophore is summarized in B and C.⁵

In those compounds containing an α -proton (I-V, all fixed *s-trans* systems), the α -proton resonance suffers a *small* shift to low field upon cooling the toluene-*d*₈

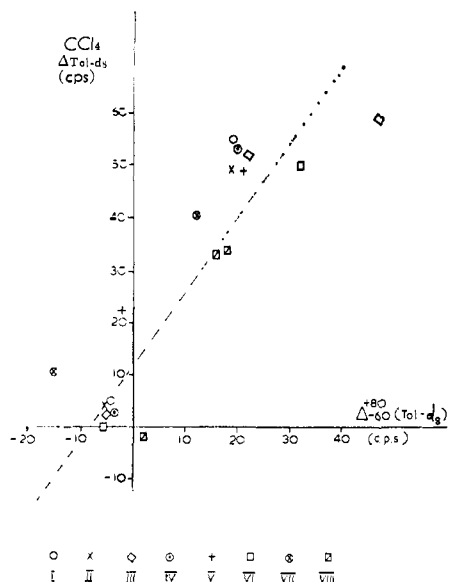


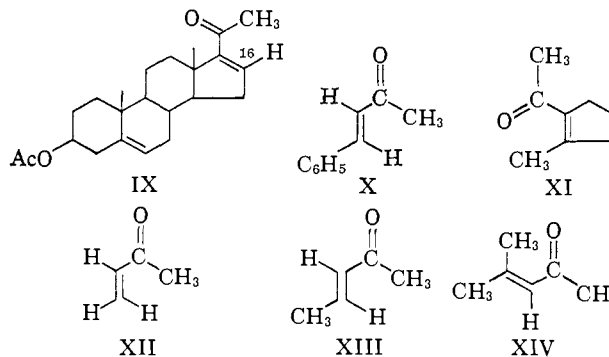
Figure 9. Plot of solvent shifts ($\Delta_{\text{Tol-d}_3}^{\text{CCl}_4} = \delta_{\text{CCl}_4} - \delta_{\text{Tol-d}_3}$) against supplementary shifts (Δ_{-80}^{+80}) induced on cooling in toluene- d_3 from $+80$ to -80° for some α,β -unsaturated ketones (I-VIII).

solution (see Figures 1-5). In contrast, the β -proton (*trans*) resonances of I and VI undergo large upfield shifts on decreasing the temperature (see Figures 1 and 6). Similarly, the α - CH_3 resonance of VI suffers a *small* shift to low field with decreasing temperature (Figure 6), whereas the β - CH_3 (*trans*) resonances of II-V undergo large upfield shifts (Figures 2-5). By far the largest shift of all is observed for the β - CH_2 (*cis*) resonance of isophorone (III) which moves to high field by no less than 0.60 ppm on decreasing the temperature of the solution from $+80$ to -80° . The widely differing shifts observed for protons in the same molecule are consistent with complex formation as noted previously.⁹ The shifts follow the empirical rule referred to previously,²⁻⁵ with the additional comment that the small or zero temperature variations anticipated for α -H resonances (these protons lie approximately in the reference plane) in I-V turn out to be slightly negative.⁹ The rule is also obeyed for the *s-cis* model compound *trans*-2-ethylidenecyclohexanone (VII), in which the β -H (*cis*) substituent is deshielded and the β - CH_3 (*trans*) substituent shielded with a temperature decrease (Figure 7). The β - CH_3 (*trans*) substituent of pulegone (VIII) shows the anticipated positive temperature variation, but somewhat surprisingly the β - CH_3 (*cis*) resonance of VIII shows no significant temperature variation whereas a small negative shift was expected. As in the case of some saturated steroidal ketones⁸ there is a correlation between the Δ values ($\Delta = \delta_{\text{CCl}_4} - \delta_{\text{Tol-d}_3}$ ppm) at normal probe temperatures and the *supplementary* shifts ($\Delta_{-80}^{+80} = \delta_{\text{Tol-d}_3}^{+80} - \delta_{\text{Tol-d}_3}^{-80}$) produced on cooling; this correlation is indicated in Figure 9. However, the correlation is in a poor one and indicates that the supplementary shifts produced on cooling are only very roughly proportional to the Δ values. An accurate proportionality would hold only if the Δ values were solely due to complex formation and if the temperature variation in toluene- d_3 produced changes in chemical

(9) By analogy to Δ values, a "negative" temperature variation is defined in terms of a shift to low field with a decrease in temperature.

shifts solely due to a change in the mole fraction of ketone complexed. As might be anticipated, Figure 9 indicates that such a picture is grossly oversimplified, but does serve to illustrate that large solvent shifts are usually associated with a marked temperature dependence, whereas small solvent shifts are usually associated with a small temperature dependence (*i.e.*, the interpretation of solvent shifts and variable-temperature shifts in terms of complex formation is a realistic approximation to the truth).¹⁰ It is also noteworthy that the α -H shifts observed for I-IV are sensibly independent of the structural variations among these compounds ($\Delta_{-80}^{+80} = -0.04, -0.05, -0.05,$ and -0.04 ppm, respectively), as are the β - CH_3 (*trans*) shifts of II, III, and IV ($\Delta_{-80}^{+80} = +0.19, +0.20, +0.20$ ppm, respectively). A larger variation is, however, observed in the β -H (*trans*) shifts for I and VI ($+0.20$ and $+0.32$ ppm, respectively).

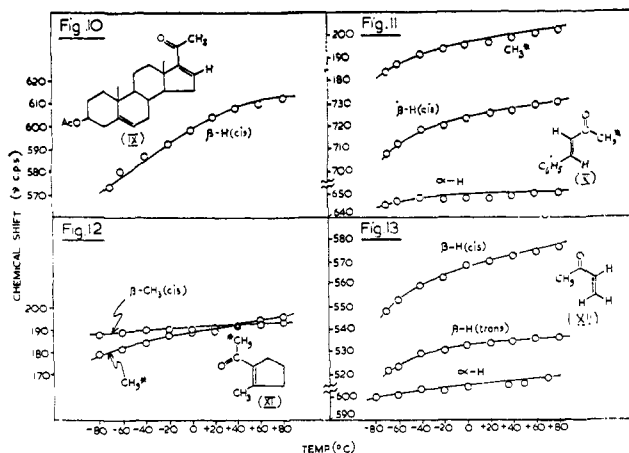
The technique outlined above is obviously useful for distinguishing between protons (or methyl groups) attached to the α - or β -carbon atoms of α,β -unsaturated ketones and should therefore prove to be of structural utility. The application of the data from fixed *s-cis* or *s-trans* systems to conformational analysis in mobile systems is outlined in the following discussion.



The mobile systems (*i.e.*, those which can exist in *s-cis* or *s-trans* conformations) examined are $\Delta^{5,16}$ -pregnadien-3 β -ol-20-one acetate (IX), *trans*-4-phenylbut-3-en-2-one (X), 1-acetyl-2-methylcyclopent-1-ene (XI), but-3-en-2-one (XII, methyl vinyl ketone), *trans*-pent-3-en-2-one (XIII), and 3-methylpent-3-en-2-one (XIV, mesityl oxide). The temperature variable shifts are summarized in Figures 10-15. In those cases where a compound is a mixture of *s-cis* and *s-trans* conformers of similar energy, the conformer populations will of course also change with temperature, but it will be seen that the over-all shapes of the curves will usually indicate which conformer is energetically most favorable (*i.e.*, which conformer is present in greater amount).

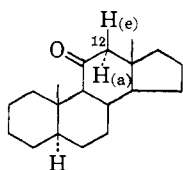
The curves presented in Figure 15 immediately show that mesityl oxide (XIV) exists very predominantly in the *s-cis* conformation. There is a very close similarity between the curves for the β - CH_3 (*cis*) and β - CH_3 (*trans*) resonances of mesityl oxide (XIV, Figure 15) and pulegone (VIII, Figure 8). In particular, the β -

(10) Attention is drawn to the fact that the α -H resonances of the cyclohexanones I-IV have small positive $\Delta_{\text{tol-d}_3}^{\text{CCl}_4}$ values (contrast their small negative temperature gradients), but that the corresponding $\Delta_{\text{CCl}_4}^{\text{CCl}_4}$ values for III and 2 other cyclohexanones are small and negative.⁹ We have thought it desirable to point out that the solvent shifts induced by toluene and benzene are therefore significantly different, even for empirical purposes.

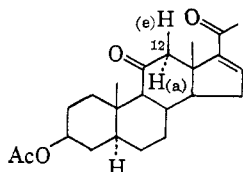


Figures 10–13. Temperature variation of the chemical shift (cps at 100 Mc) of some proton resonances of $\Delta^{5,16}$ -pregnadien-3 β -ol-20-one acetate (IX), *trans*-4-phenylbut-3-en-2-one (X), 1-acetyl-2-methylcyclopent-1-ene (XI), and but-3-en-2-one (XII), respectively.

CH_3 (*cis*) resonance is deshielded on cooling the toluene- d_8 solution, establishing its location approximately in or in front of the reference plane. The temperature dependence of this resonance is sharply contrasted with that of the $\beta\text{-CH}_2$ (*cis*) resonance of isophorone (III, fixed *s-trans*). The conclusion that the *s-cis* conformation is preferred for mesityl oxide is in agreement with previous studies.^{5,11–14} Similarly, the very marked downfield shift of the 16-H resonance of $\Delta^{5,16}$ -pregnadien-3 β -ol-20-one acetate (IX, Figure 10) establishes that the 16-en-20-one chromophore prefers the *s-trans* conformation. This conclusion is substantiated by a comparison of the Δ values ($\Delta = \delta_{\text{CDCl}_3} - \delta_{\text{C}_6\text{H}_6}$, ppm)¹⁵ for 5 α -androstan-11-one (XV) and for Δ^{16} -pregnen-3 β -ol-11,20-dione acetate (XVI) which are given with the structural formulas below. Both Δ values for the C-12 protons become more negative on passing from XV to XVI, and so it must be concluded



$$\text{XV}, \Delta(12\beta\text{-H, equatorial}) = -0.03 \\ \Delta(12\alpha\text{-H, axial}) = +0.37$$



$$\text{XVI}, \Delta(12\beta\text{-H, equatorial}) = -0.26 \\ \Delta(12\alpha\text{-H, axial}) = +0.16$$

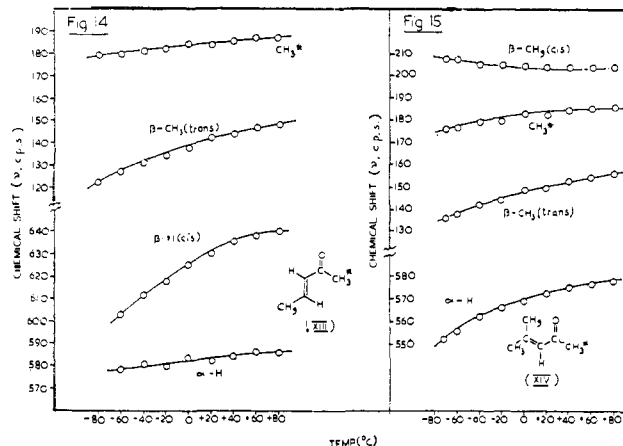
(11) C. J. Timmons, B. P. Straughan, W. F. Forbes, and R. Shilton in "Advances in Molecular Spectroscopy," Vol. 2, A. Mangini, Ed., Pergamon Press, Oxford, 1962, p 933.

(12) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2201 (1961).

(13) J. B. Bentley, K. E. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949).

(14) J. E. Baldwin, *J. Org. Chem.*, **30**, 2423 (1965).

(15) N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 173.



Figures 14 and 15. Temperature variation of the chemical shift (cps at 100 Mc) of some proton resonances of *trans*-pent-3-en-2-one (XIII) and 3-methylpent-3-en-2-one (XIV).

that these protons lie in front of the C-20 carbonyl group (*i.e.*, that the 16-en-20-one chromophore prefers the *s-trans* conformation).

The observation that the $\beta\text{-CH}_3$ (*cis*) resonance of 1-acetyl-2-methylcyclopent-1-ene (XI) is barely dependent on temperature illustrates that this compound exists largely in the *s-cis* conformation drawn in Figure 12 (compare the similarity of the $\beta\text{-CH}_3$ (*cis*) resonance curves in Figures 8 and 12, but contrast these curves with that observed for the $\beta\text{-CH}_2$ (*cis*) resonance of isophorone (III, Figure 3)); this conclusion is in agreement with that based on infrared spectroscopy.¹⁶

Any conformational preference in the remaining labile α,β -unsaturated ketones (X, XII, XIII) is less clearly defined by the variable-temperature studies.¹⁷ The small upfield shifts of the $\alpha\text{-H}$ resonances with decreasing temperature in each case (Figures 11, 13, and 14, respectively) suggest that these compounds do not exist solely in the *s-trans* conformations, but on the other hand the marked upfield shifts of the $\beta\text{-H}$ (*cis*) resonances establish the presence of a large proportion of the *s-trans* conformer. The sharp dips in these latter curves for X (Figure 11) and XII (Figure 13) at lower temperatures (-40 to -80°) point to an increase of population of *s-trans* forms on cooling (*i.e.*, that these compounds are mixtures of the two possible forms at room temperature but that the *s-trans* form is slightly energetically favored). In fact, infrared and Raman data have been interpreted to indicate that *trans*-4-phenylbut-3-en-2-one (X), but-3-en-2-one (XII), and *trans*-pent-3-en-2-one (XIII) all exist as mixtures of *s-cis* and *s-trans* isomers at room temperature.^{11,16,18–20}

In conclusion, it may be said that the temperature dependence of proton resonances in the spectrum of an α,β -unsaturated ketone in toluene- d_8 may be used to indicate the average location of protons relative to the carbonyl group. In the fixed enone systems which have been studied, α substituents (H, CH_3) on the double bond can be readily differentiated from the

(16) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(17) The spectrum of methyl vinyl ketone (XII) was analyzed with the aid of the spectrum of 1,1,1,3,3,3-hexafluoro-2-but-3-en-2-one ($\text{CD}_3\text{COCD}=\text{CH}_2$).

(18) R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).

(19) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2225 (1961).

(20) M. E. Kronenberg and E. Havinga, *Rec. Trav. Chim.*, **84**, 17 (1965).

corresponding β substituents, while in mobile systems the conformational preference of the chromophore may be indicated.

Experimental Section

The nuclear magnetic resonance spectra were determined using a Varian HA-100 spectrometer equipped with variable-temperature probe. The variable-temperature system was calibrated by measuring peak separations in the spectrum of ethylene glycol (for the range $+60$ to $+100^\circ$) or in the spectrum of methanol (for the range -80 to $+60^\circ$); the specified calibration accuracy is $\pm 3^\circ$. Peak positions were measured directly from calibrated paper, after checking the calibration using a frequency counter (Advance, timer counter Type TC2A) immediately before each run was performed.

Resonance positions were measured relative to an internal tetramethylsilane reference. The spectra of all the compounds were determined using dilute solutions (2–5% w/v) in carbon tetrachloride or in toluene- d_6 ; the latter solvent was obtained from Merck Sharp and Dohme, Montreal. Spectral analysis was carried out using the first-order method; analysis of the ABC system of but-3-en-2-one (XII) was aided by the spectrum of 1,1,1,3- d_4 -but-3-en-2-one.

Acknowledgments. J. R. is grateful for the award of an SRC postgraduate studentship. We wish to thank Mr. M. Karger and Dr. I. Fleming for a sample of 1,1,1,3- d_4 -but-3-en-2-one. Thanks are expressed to Dr. A. F. Thomas (Firmenich et Cie, Geneva) for a generous gift of 3-methylcyclohexenone.

Structural Elucidation and High-Resolution Mass Spectrometry of Gaillardin, a New Cytotoxic Sesquiterpene Lactone

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Contribution from the Department of Pharmaceutical Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and the Space Sciences Laboratory and Department of Chemistry, University of California, Berkeley, California. Received June 15, 1966

Abstract: Evidence is presented for assignment of structure **6** to gaillardin. Elemental analysis and high-resolution mass spectrometry supported a $C_{17}H_{22}O_5$ molecular formula for gaillardin. Chemical and spectral evidence indicated the presence of α,β -unsaturated lactone, acetate ester, tertiary hydroxyl, and isolated double-bond groupings. The perhydroazulene ring system was indicated by dehydrogenation to chamazulene (**7**). Partial hydrogenation or sodium borohydride reduction of gaillardin (**6**) gave dihydrogaillardin (**9**), and epoxidation of **9** gave dihydroepoxygaillardin (**12**). Alkaline hydrolysis of **9** afforded desacetyldihydrogaillardin (**11**) and oxidation of **11** gave desacetyldihydrodehydrogaillardin (**14**). Dehydration of **14** gave dienones **13** and **15**. Treatment of gaillardin (**6**) with aqueous methanolic potassium carbonate gave 13-methoxydesacetylgaillardin (**5**); hydrolysis in aqueous dioxane gave desacetylgaillardin (**8**). Catalytic hydrogenation of gaillardin (**6**) gave tetrahydrogaillardin (**10**). Low- and high-resolution mass spectra of gaillardin (**6**) and a number of its derivatives (**5**, **8**, **9**, **11**, **12**, and **14**) are presented and discussed. The mass spectra of the desacetyl derivatives **8** and **11** are interpreted in detail.

Gaillardin is a cytotoxic sesquiterpene lactone from *Gaillardia pulchella* Foug., and its isolation and preliminary characterization have recently been reported.^{6,7} It is the purpose of this paper to present in

detail the structural elucidation and high-resolution mass spectrometry of gaillardin (**6**). Gaillardin appears to be the first normal guaianolide derivative isolated from *Gaillardia* species.

The molecular formula, $C_{17}H_{22}O_5$, was assigned for gaillardin on the basis of elemental analysis and high-resolution mass spectrometry. The presence of high intensity end absorption in the ultraviolet absorption spectrum and of bands at 5.67 and 6.00 μ in the infrared absorption spectrum suggested the presence of an α,β -unsaturated lactone group **1**. The latter grouping is also found in other constituents of *Gaillardia* species.^{8–10} The presence of an acetate grouping, indicated by the molecular formula and the infrared absorption at 5.78 and 8.15 μ , was supported by the presence of a characteristic $M - 60$ peak at m/e 246 in the mass spectrum of gaillardin. The infrared (2.78 μ) and mass ($M - 18$ peak) spectra also indicated the presence of a hydroxyl group. The resistance of the hydroxyl group toward attempted acetylation with acetic anhydride—

(1) University of Wisconsin. This is part XVII in the series entitled "Tumor Inhibitors." Part XVI is: S. M. Kupchan, Y. Aynehchi, J. M. Cassady, A. T. McPhail, G. A. Sim, H. K. Schnoes, and A. L. Burlingame, *J. Am. Chem. Soc.*, **88**, 3674 (1966). The investigation at the University of Wisconsin was supported in part by grants from the National Institutes of Health (CA-04500) and the American Cancer Society (T-275).

(2) National Institutes of Health Postdoctoral Fellow, 1965–1966.

(3) University of California. This is part VIII in the series entitled "High Resolution Mass Spectrometry in Molecular Structure Studies." Part VII: A. L. Burlingame, R. W. Olsen, K. L. Pering, H. M. Fales, and R. J. Highet, in preparation. The investigation at the University of California was supported in part by a grant from the National Aeronautics and Space Administration (NsG 101).

(4) National Institutes of Health Predoctoral Fellow, 1965–1966.

(5) National Aeronautics and Space Administration Predoctoral Fellow, 1965–1966.

(6) S. M. Kupchan, J. M. Cassady, J. Bailey, and J. R. Knox, *J. Pharm. Sci.*, **54**, 1703 (1965).

(7) Roots, stems, leaves, and flowers were collected 8–9 miles southwest of George West along Route 59, Live Oak County, Texas, on April 13, 1964. The authors acknowledge with thanks receipt of the dried plant material from Dr. Robert E. Perdue, Jr., U. S. Department of Agriculture, Beltsville, Md., in accordance with the program developed with the U. S. D. A. by the Cancer Chemotherapy National Service Center.

(8) W. Herz, K. Ueda, and S. Inayama, *Tetrahedron*, **19**, 483 (1963).

(9) W. Herz and S. Inayama, *ibid.*, **20**, 341 (1964).

(10) W. Herz, S. Rajappa, M. V. Lakshmikantham, and J. J. Schmid, *ibid.*, **22**, 693 (1966).