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# Proton Magnetic Resonance Studies of Enolised β-Triketones

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Triacetylmethane together with some 2-acyl*cyclo*hexane-1,3-diones and the fern pigment ceroptene and its transformation products have been investigated by proton magnetic resonance (PMR) and infrared spectroscopy.

In the PMR spectra, very large shifts ($-\delta_{aq}$ = 12.6–14.1) were observed for the enolic protons, the largest shifts being shown by the conjugated β-triketones. The shifts were correlated with the infrared chelate carbonyl absorptions.

The results indicate that, in solution, ceroptene is present as a mixture of two enol forms of 5-methoxy-2-cinnamoyl-6,6-dimethyl-*cyclo*hex-4-ene-1,3-dione (IV, R = Ph–CH=CH–).

Interest in β-triketones (α-acyl-β-diketones) has been mainly devoted to the 2-acyl*cyclo*hexane-1,3-diones and -1,3,5-triones. These types of β-triketones form an important group of natural products; *cf.* the recent review by Hassall [1].

Our interest in this type of compound arose from work on the natural colouring matter of the fern *Pityrogramma triangularis*. This pigment, ceroptene, was recently investigated by one of us and was shown to be a methyl enol ether of 2-cinnamoyl-6,6-dimethyl*cyclo*hexane-1,3,5,-trione (III, R=Ph–CH=CH–), either 5-methoxy-2-cinnamoyl-6,6-dimethyl*cyclo*hex-4-ene-1,3-dione (IV,R = Ph–CH = CH–) or 3-methoxy-2-cinnamoyl-6,6-dimethyl*cyclo*hex-3-ene-1,5-dione (V, R = Ph–CH = CH–) [2]. Of these, structure IV was considered more likely since the infrared data indicated a pronounced conjugated chelation (*cf.* discussion below) similar to that suggested by Chan and Hassall [3] for 2-acyl*cyclo*hexane-1,3-diones. However the chelate carbonyl absorption (1 515 $cm^{-1}$) occurred at a lower frequency than any previously reported and it was considered desirable to check this assignment by some independent method.

An opportunity arose of studying this problem by nuclear magnetic resonance as part of the general hydrogen bond research programme of the NMR group at this institute.

To provide background information a survey was made of the hydrogen bonding of some simple $\beta$-triketones as well as of ceroptene and its transformation products. The basic compound of the series, triacetylmethane (I), was prepared in a state of purity. 2-Acetyl-5,5-dimethyl*cyclo*hexane-1,3-dione ("acetyldimedone", II, R = $CH_3$) which was readily accessible by synthesis was taken as a convenient model compound for ceroptene, especially since condensation with aromatic aldehydes afforded conjugated analogues.

## METHODS

*Proton magnetic resonance measurements.* The measurements were made with a Varian V—4 300 NMR spectrometer operating at a fixed frequency of 40 Mc/s and equipped with a Varian V-K 3 506 Super Stabilizer.

The sample cells used in all low concentration measurements were thin-walled glass tubes with a good filling factor [4]. Measurements against an external water standard were made in coaxial glass tubes containing water in the central capillary and the solution to be measured in the annular space. Using the notation of Reilly, McConell and Meisenheimer [5], the concentric tube had the following dimensions: $2\,a = 1.3$ mm, $2\,b = 1.8$ mm and $2\,r = 2.45$ mm.

The resonance shifts were determined in c/s by the audiofrequency sideband method employing a Hewlett-Packard 200 CD Audio Oscillator. The sign of the shift was taken as positive when the resonance occurred at a higher field than that of the water reference. The shift measurements were generally reproducible to within $\pm$ 1 c/s.

Resonance shifts are sometimes discussed in terms of the dimensionless unit $\delta$ defined by the expression

$$\delta = 10^6 \frac{H_{\text{sample}} - H_{\text{ref}}}{H_{\text{ref}}}$$

To avoid confusion, the reference substance is specified here by a lower index, *e.g.* $\delta_{aq}$.

Where not otherwise stated the sample temperature was 22 $\pm$ 1°. For the measurement at —30°, an apparatus permitting simultaneous cooling and spinning of the sample was employed.

As has been pointed out by Allred and Rochow [6], diamagnetic anisotropy effects in the interaction between solvent and solute may introduce errors and make the direct comparison of different PMR spectra less satisfactory. Thus benzene is known to cause solvent shifts that vary with the nature of the solute. This is probably due to the magnetic anisotropy effects of the benzene ring [7]. The PMR shifts of all compounds were therefore determined using dilute carbon tetrachloride solutions against an external water standard in order to keep the bulk diamagnetic susceptibility practically constant in all measurements and, also, to eliminate to some extent the anisotropy effects of the solvent.

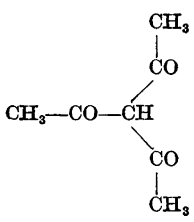
*Infrared measurements.* The infrared spectra were recorded on a Perkin-Elmer No 21 instrument using a sodium chloride prism, carbon tetrachloride solutions (*ca.* 0.1 M) and rock salt cells of 0.1 and 1 mm thickness. The solvent absorption was compensated with a Hilger-Watts variable cell. The calibration of the wavelength scale was checked against atmospheric moisture. The frequencies should be accurate to within $\pm$ 5 $cm^{-1}$. The sample temperature was *ca.* 25°.

## MATERIALS

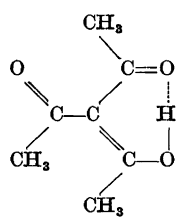
*Solvents.* For the PMR measurements, carbon tetrachloride (*Merck pro analysi*) was dried over phosphorus(V)oxide and distilled. The benzene used was a redistilled product (*Merck pro analysi*). For the IR measurements, commercial carbon tetrachloride as above was used without further treatment.

*Triketones.* Melting points were determined on a Kofler block.

*3-Acetylpentane-2,4-dione* (»triacetylmethane», I). Since there is some discussion in the literature about this compound, the detailed experimental procedure will be given.



a



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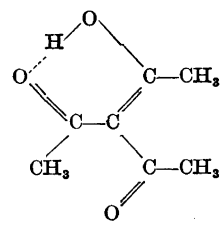

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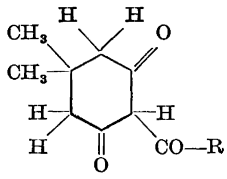
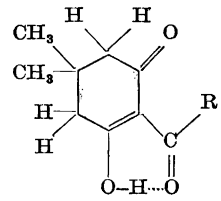
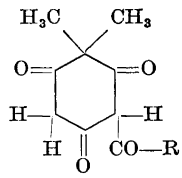
I





II



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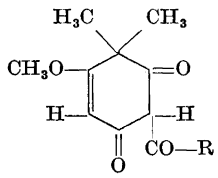

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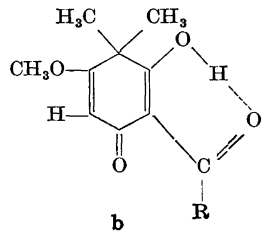

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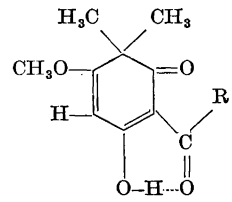

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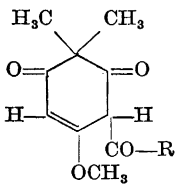
IV



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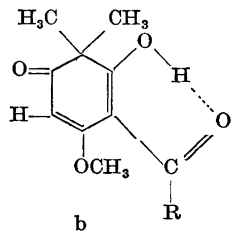

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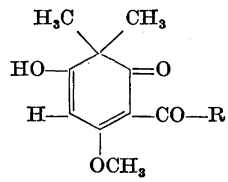

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V

A suspension of sodium hydride (1 mole, 50 % in paraffin oil) in dry ether (1 000 ml) was cooled to 0° and acetylacetone (1 mole) in ether (100 ml) was added during 30 min. When hydrogen evolution had ceased, acetyl chloride (1 mole) in ether (100 ml) was added during 30 min. The reaction mixture was left overnight. Water (500 ml) was then added to dissolve the sodium chloride, and the ethereal solution obtained was washed with water and exhaustively extracted with sodium hydrogen carbonate (sat.). The hydrogen carbonate extract was washed thoroughly with ether to remove all traces of neutral material, acidified with dilute sulphuric acid and the triacetylmethane was extracted with ether. The ether extract was washed with several portions of water, dried and evaporated giving crude triacetylmethane (*ca.* 20—25 %) in which no enol acetate could be detected (IR). Distillation gave pure triacetylmethane in 15—20 % yield. For the NMR and IR measurements a fraction was taken of b.p. 85—86°/7 mm, $n_D^{25}$ 1.4893, $d_4^{20}$ 1.096, equiv. wt. 142 (by titration with standard alkali against phenolphtalein; calc. 142). The b.p. has been given as 104°/19 mm [8,9] and the density as $d_4^{20}$ 1.0658 and $d_4^{22}$ 1.0742 [9]. The measurements were made within 24 h of the preparation because of the instability of the compound.

The ether phase remaining after the hydrogen carbonate extraction contained neutral material (*ca.* 60 g, excluding paraffin), which according to its IR spectrum (compare Rasmussen *et al.*[10]), consisted mainly of the enol acetate of acetylacetone. This decomposed both on distillation and on extraction with 2 M sodium hydroxide. Repeated extraction with sodium carbonate (5 %) gave additional quantities of triacetylmethane, thus indicating that the enol acetate is slowly converted to the triketone.

Essentially the same results were obtained using powdered sodium. This shows the correctness of the original work by Nef [8] and also indicates the cause of the aberrant results of Birkenbach *et al.*[9] (see also Schwarzenbach and Lutz [11]).

*2-Acetyl-5,5-dimethyl*cyclo*hexane-1,3-dione* ("acetyldimedone", II, R = $CH_3$) was prepared according to Dieckmann and Stein [12]. It was purified *via* the copper salt and then distilled, b.p. 132—133°/20 mm, m.p. 36—38°. The authors cited give m.p. 36°.

*2-Cinnamoyl-5,5-dimethyl*cyclo*hexane-1,3-dione* ("cinnamoyldimedone", II, R = Ph—CH=CH—) was prepared by condensation of acetyldimedone with benzaldehyde on the water bath for 1 h using piperidine as catalyst. The product was distilled, b.p. *ca.* 190°/1 mm, and recrystallised from methanol, m.p. 98—100°. Ukita *et al.*[13] report m.p. 96.5°. Yield 50 %.

*2-Hydrocinnamoyl-5,5-dimethyl*cyclo*hexane-1,3-dione* (II, R = Ph—$CH_2$—$CH_2$—) was obtained in 70 % yield from cinnamoyldimedone by hydrogenation over palladised charcoal in ethanol. It was recrystallised from *cyclo*hexane and sublimed, m.p. 57—58.5°. (Found: C 74.9; H 7.4. Calc. for $C_{17}H_{20}O_3$: C 75.0; H 7.4.)

*2-(4-Methoxycinnamoyl)-5,5-dimethyl*cyclo*hexane-1,3-dione* was obtained from acetyldimedone and anisaldehyde using piperidine as catalyst. It was recrystallised from methanol and sublimed, m.p. 136—138°. Yield 60 %. (Found: C 71.8; H 6.6. Calc. for $C_{18}H_{20}O_4$: C 72.0; H 6.7.)

*2-(4-Methoxyhydrocinnamoyl)-5,5-dimethyl*cyclo*hexane-1,3-dione* was prepared, in 60 % yield, by hydrogenation of the above compound. It was recrystallised from *cyclo*hexane and sublimed, m.p. 71—72.5°. (Found: C 70.8; H 7.4. Calc. for $C_{18}H_{22}O_4$: C 71.5; H 7.3.)

For details of the ceroptene derivatives, *cf.* Ref.[3]

*O-Methyl-3-acetylfilicinic acid.* A synthetic product was recrystallised from *cyclo*hexane and sublimed, m.p. 107—109°.

*Dihydroceroptene* was obtained by hydrogenation of the natural product. It was recrystallised from methanol, m.p. 98—100°.

*Ceroptene.* Samples of the natural product were recrystallised from methanol, m.p. 137—140°.

## RESULTS

### Proton magnetic resonance measurements

*Triacetylmethane* (I). Investigations by Schwarzenbach and Lutz [11] indicate that this compound is completely enolised in aqueous solution. As indicated

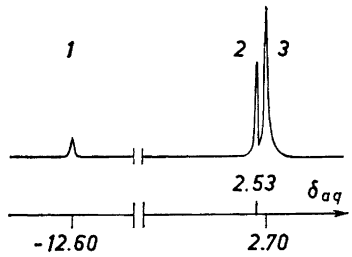


*Fig. 1.* PMR spectrum of triacetylmethane in carbon tetrachloride (mole fraction $x = 0.1$). Chemical shifts given as $\delta_{aq}$.

above, the "triketo form" discussed by Birkenbach *et al.* [9] is apparently the enol acetate of acetylacetone. The PMR spectrum of the pure liquid showed a minor peak ($\delta_{aq} = 0.3$) which may be due to the central hydrogen atom of the triketo form and corresponds to the presence of *ca.* 5 % of non-enolised material. This signal could not be detected in the spectra of the solutions and it may be concluded that triacetylmethane is almost completely enolised in solution. In the IR spectrum of the pure liquid, there was a shoulder at 1 700 $cm^{-1}$, possibly also due to the triketo form.

The PMR spectrum of the carbon tetrachloride solution was simple (Fig. 1). Signal 1 was assigned to the enolic proton. The chemical shift was large ($\delta_{aq} = -12.6$) compared with that for acetylacetone ($\delta_{aq} = -10$, *cf.* Reeves [14]). In acetylacetone, the methyl groups are identical in the PMR spectrum and Reeves has attributed this to the rapid movement of the enolic proton along the hydrogen bond. In the PMR spectrum of triacetylmethane, there were two methyl signals (2 and 3) and the intensity ratio was 1:2. Signal 2 was attributed to the methyl group not directly attached to the hydrogen bond system and signal 3 to the two methyl groups adjacent to the intramolecular hydrogen bond. The existence of two separate methyl signals indicated that the interconversion of identical forms (for instance I b and c) was slow.

In benzene solution the methyl signals coincided. This may be due to a solvent anisotropy effect or to the rapid interconversion of identical forms. It was interesting to note that the enol proton signal occurred at a still lower field ($\delta_{aq} = -13.1$).

*Acetyldimedone* (II, R = $CH_3$). This compound is known to be completely enolised in both polar and non-polar solvents [3].

The PMR spectra of solutions in carbon tetrachloride, benzene and a mixture of these solvents are shown in Fig. 2. Signal 1 in the first spectrum was considered to be due to the enolic proton. The chemical shift was larger than that for triacetylmethane ($\delta_{aq} = -13.3$). Signal 4 was evidently caused by the gem-dimethyl group since the chemical shift was close to the expected value and the intensity corresponded to six of the fourteen protons. Signal 3 ($\delta_{aq} = 2.69$) judging by its intensity, should correspond to two protons and should therefore be due to a ring methylene group. Signal 2 was at first difficult to explain. The intensity indicated, however, that it was due to five protons. In benzene solution, the magnitudes of peaks 2 and 3 were reversed and, in mixtures of these solvents, they were resolved into three peaks with relative intensities 3:2:2. This clearly indicated that peak 2 in the first spectrum was

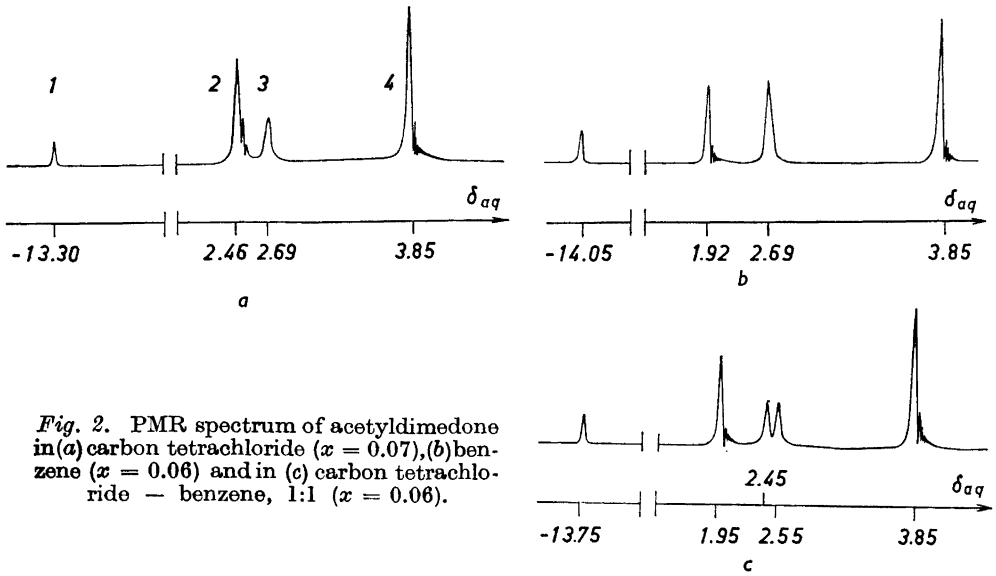


*Fig. 2.* PMR spectrum of acetyldimedone in (*a*) carbon tetrachloride ($x = 0.07$), (*b*) benzene ($x = 0.06$) and in (*c*) carbon tetrachloride — benzene, 1:1 ($x = 0.06$).

the sum of signals from the acetyl group and one methylene group. In the PMR measurements on the benzene solution, the methylene groups were equivalent; this is analogous to the results obtained with triacetylmethane. The separation of signals 2 and 3 in the carbon tetrachloride solution was not affected by lowering the sample temperature to −30°.

*Hydrocinnamoyldimedone* (II, R = Ph—$CH_2$—$CH_2$—). The PMR spectrum (Fig. 3) was clearly reminiscent of that of acetyldimedone. The protons of the benzene ring and the methylene groups between the rings gave signals at the expected field (signals 2 and 3). The enol proton signal (1) occurred at the same field as in acetyldimedone. Approximately the same splitting and shifts for the methylene groups in the ring (4) were recognised.

*Cinnamoyldimedone* (II, R = Ph—CH = CH—). In the spectrum for this compound (Fig. 3), the enolic proton appeared as a signal at a very low field ($\delta_{aq} = -13.8$). The gem-dimethyl group gave a signal at the same field as in acetyldimedone (5) and the methylene signals (4) were quite separate. Signal group 2, consisting of two signals of high intensity ($\delta_{aq} = -3.23$ and $-3.10$,) and two signals of lower intensity ($\delta_{aq} = -3.80$ and $-2.70$ hidden in signal group 3), possessed the characteristic appearance of two spin-coupled non-identical protons of a —CH = CH— group [15]. The spin-coupling constant, $J$, was 15 c/s, indicating *trans*-configuration [16]. The PMR spectrum of ethyl cinnamate ($x = 0.1$ in carbon tetrachloride) was recorded for comparison. It showed a spin-coupling constant for the *trans*-ethylenic double bond protons of 16.0 c/s.

The benzenoid protons in cinnamoyldimedone gave a complex signal (3) of the type often obtained from conjugated aromatic nuclei.

4-Methoxycinnamoyldimedone and its dihydroderivative showed no relevant differences and the enol proton resonances occurred at the same fields as those for cinnamoyldimedone and hydrocinnamoyldimedone respectively.

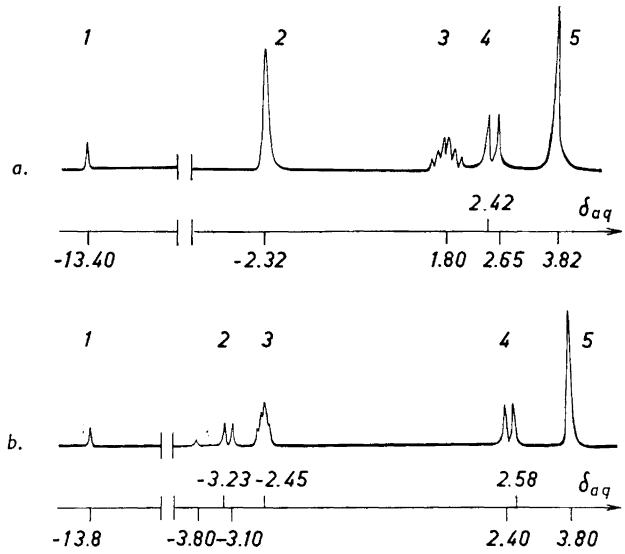


*Fig. 3.* PMR spectra of (*a*) hydrocinnamoyldimedone ($x = 0.05$) and (*b*) cinnamoyldimedone ($x = 0.04$) in carbon tetrachloride.

*O-Methyl-3-acylfilicinic acids.* It was shown previously [2] that ceroptene is a methyl ether of 3-cinnamoylfilicinic acid (III, R = Ph—CH = CH—).

3-Acylfilicinic acids could give several methyl ethers; only two are however capable of giving enols with strong intramolecular hydrogen bonds (IV and V). The ether indicated in formula IV in addition to the wholly ketonic form, might also give two different conjugated chelate enols (IV b and c). The ether indicated in V can only give one enol stabilised by strong intramolecular hydrogen bonding (V b). The other form (V c) is of the dimedone type and is unlikely to be present in appreciable amounts in dilute solutions in non-polar solvents. As discussed under triacetylmethane, the movement of protons along the hydrogen bond is very rapid and the corresponding additional forms need no separate discussion.

In previous work [2], it was shown that in ceroptene, dihydroceroptene and O-methyl-3-acetylfilicinic acid the methoxyl group has the same position and thus a choice has to be made between structures IV and V.

*O-Methyl-3-acetylfilicinic acid* (R = $CH_3$). The PMR spectrum is shown in Fig. 4. There are five main bands, four of which have small side bands. The ratio of the intensities of side and main bands was fairly constant — 1:6. In benzene solution, the splitting persisted although the side bands were smaller — the intensity ratio was 1:8. The most reasonable explanation for the splitting seems to be that two tautomeric forms are present and that these forms are very similar but not rapidly interconvertible. A change of solvent is likely to change the equilibrium proportions and the rate of interconversion but apparently this rate is low even in benzene. Assignments will be made without reference to the splitting.

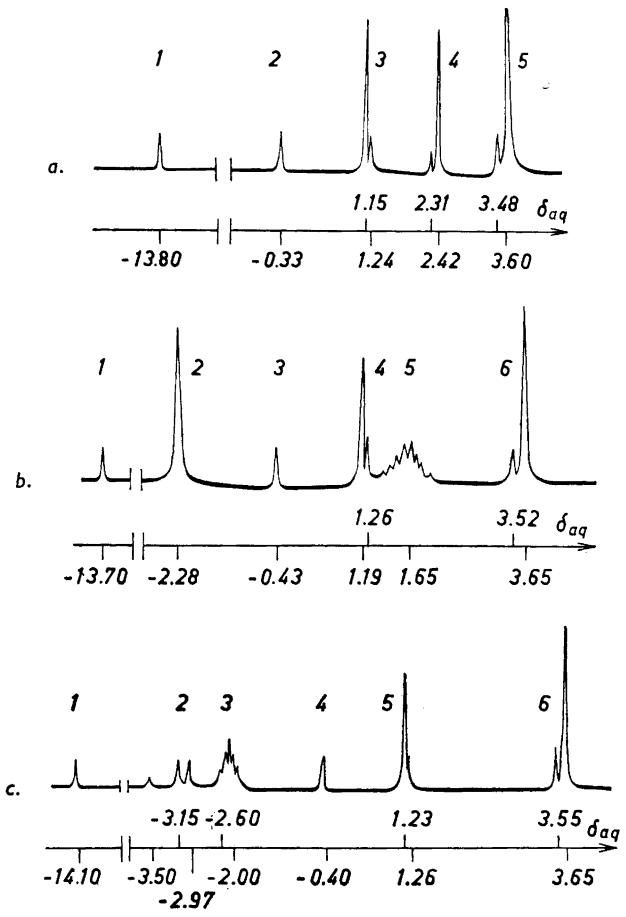


*Fig. 4.* PMR spectra of (*a*) O-methyl-3-acetylfilicinic acid ($x = 0.05$), (*b*) dihydroceroptene ($x = 0.06$) and (*c*) ceroptene ($x = 0.03$) in carbon tetrachloride.

Signal 1 was found at a very low field ($\delta_{aq} = -13.8$). It was undoubtedly due to the enolic proton. Signal 2 was assigned to the $-CH =$ group of the filicinic acid ring because of the chemical shift and the intensity. Signal 3 was considered to be due to the methoxyl protons. A change of solvent brings about a remarkable displacement of the resonance field ($\delta_{aq} = 1.05$ in carbon tetrachloride solution to $\delta_{aq} = 1.89$ in benzene solution; $\Delta\delta = 0.84$). Similar solvent-dependent shifts have, however, also been observed with aromatic methyl ethers, *e.g.* anisole and guaiacol ($\Delta\delta \approx 1.0$). Signal 4 was assigned to the acetyl group by analogy with acetyldimedone. Signal 5 was found to have approximately double the intensity of signals 3 or 4. Its position in the high field side of the spectrum provided further evidence that it was caused by the gem-dimethyl grouping.

*Dihydroceroptene* (R = Ph—$CH_2$—$CH_2$—). Apart from the "isolated" benzene ring, this compound is analogous to O-methyl-3-acetylfilicinic acid as shown by the almost identical ultraviolet spectra [2]. The similarities recur also in the PMR spectra (Fig. 4). The same splitting of the signals can be observed and the ratio of side band to main band is close to that for the previous compound (1:5). This indicates that the splitting is not due to impurities since the dihydroceroptene was obtained from the natural product whereas the O-methyl-3-acetylfilicinic acid was an independent synthetic product and the same amount and type of impurities cannot be expected to be present in both. In benzene solution, the intensity ratio was 1:4.5.

Signal 1 ($\delta_{aq} = -13.7$) was considered to be due to the enolic proton while signal 2 was assigned to the protons of the benzene ring and peak 3 to the —CH = group of the filicinic acid ring. Signal 4 was caused by the methoxyl group and showed the same solvent displacement as that discussed above. Signal 5 was composed by a number of peaks and undoubtedly was due to the methylene groups between the rings. Signal 6 was due to the gem-dimethyl group.

*Ceroptene* (R = Ph—CH = CH—). The splitting effects in this spectrum were slightly more marked than those in the two compounds above and the ratio was *ca.* 1:4. No splitting of signal 4 was observed but this was probably due to the low concentration. Ceroptene is not very soluble in carbon tetrachloride and this made it necessary to operate the spectrometer at the sensitivity limit. There was no appreciable splitting of the signals in benzene solution, which may indicate that one of the forms predominates.

Signal 1 was assigned to the enolic proton — it occurred at the lowest field yet reported for a proton resonance signal ($\delta_{aq} = -14.1$).* Signal group 3, consisting of two signals of high intensity and two of low intensity, was analogous to signal group 2 in the spectrum of cinnamoyldimedone. It was therefore attributed to the protons at the *trans*-ethylenic double bond. The spin-coupling constant, $J$, was 16 c/s. Signal 3 was assigned to the protons of the benzene ring and signal 4 to the proton of the filicinic acid ring. Signal 5 was due to the methoxyl group — it showed a strong solvent dependence. Signal 6 was assigned to the gem-dimethyl group.

## Infrared measurements

The following list gives absorptions in the 1 500—1 700 $cm^{-1}$ region with assignments and — in brackets — the approximate molecular extinction coefficients ($mole^{-1}$ 1 $cm^{-1}$).

All compounds investigated showed a very broad absorption in the region 3 200—1 900 $cm^{-1}$. It was however weak, $\varepsilon$ *ca.* 20), and it was not possible to define a fixed hydroxyl stretching frequency. The chelate carbonyl absorptions were also rather broad and intensity comparisons could therefore be

* The proton involved in the symmetrical hydrogen bond in potassium hydrogen maleate has been found at a still lower field ($\delta_{aq} = -15.40$). Forsén, S. *J. Chem. Phys.* **31** (1959) 852.

misleading. It is not possible in these complicated spectra to make satisfactory measurements of the integrated absorption intensities.

All cinnamoyl derivatives gave absorption close to 1 310 and 970 $cm^{-1}$ due to the *trans* ethylenic double bond.

The data for ceroptene and its transformation products have been taken in part from previous work [2].

*Assignments: a* conjugated, chelated carbonyl group; *b* conjugated carbonyl group (non- chelated); *c* conjugated aromatic ring; *d* ethylenic double bond; *e* enol ether double bond; *f* aromatic ring.

*Triacetylmethane:* 1 580 a (200), 1 678 b (300).

*Acetyldimedone:* 1 560 a (200), 1 660 b (500); *cf.* Refs. [3,13]

*Hydrocinnamoyldimedone:* 1 560 a (250), 1 600 (shoulder), 1 665 b (500).

*Cinnamoyldimedone:* 1 520 a (300), 1 578 c (250), 1 615 d (500), 1 665 b (500)

p-*Methoxyhydrocinnamoyldimedone:* 1 515 f (600), 1 563 a (250), 1 610 f (250), 1 665 b (500).

p-*Methoxycinnamoyldimedone:* 1 512 f (800), 1 525 a (shoulder *ca.* 400), 1 575 c (400), 1 603 f (700), 1 620 d (500), 1 660 b (500).

*O-Methyl-3-acetylfilicinic acid:* 1 525 a (500), 1 621 e (500), 1 660 b (500).

*Dihydroceroptene:* 1 525 a (500), 1 625 e (400), 1 665 b (500).

*Ceroptene:* 1 515 a (600), 1 580 c (250), 1 625 e, d (800), 1 655 b (400).

## DISCUSSION

The concept of conjugated chelate systems was proposed by Rasmussen, Tunnicliff and Brattain [10] to cover the phenomenon of strong intramolecular hydrogen bonding and simultaneous conjugation between the electronegative atoms connected by the hydrogen bond. The term has been used mostly in connection with the interpretation of the infrared spectra of $\beta$-dicarbonyl compounds and related substances but has also been extended to cover some intermolecular hydrogen bonding phenomena, *e.g.* in the dimer of dimedone [10]. The applications have been discussed by Bellamy [18]. In the infrared spectra conjugate chelation gives rise to very broad and weak hydroxyl stretching absorptions at low frequencies (in general below 3 000 $cm^{-1}$) and to carbonyl absorption of unusual intensity shifted to a lower frequency than that for ordinary conjugated carbonyl compounds.

In the present investigation no evidence was obtained for the presence of non-enolised species of $\beta$-triketones in solution and it is evident that the $\beta$-triketones investigated are completely enolised in solution. The infrared spectra of the solid compounds in potassium bromide discs also indicated complete enolisation.

It is evident from the results obtained that the conjugated chelate system in the enolised $\beta$-triketones has rather exceptional properties, which are particularly marked in those compounds where further conjugation is present. Ceroptene appears to have the lowest proton resonance field and the lowest chelate carbonyl absorption frequency yet reported (*cf.* Reeves [14] and Bellamy [18]).

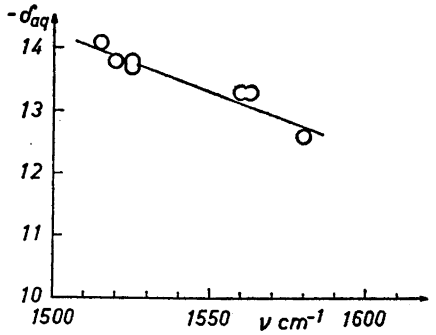


*Fig. 5.* Correlation of the PMR enol proton shift with the infrared chelate carbonyl frequency.

In Fig. 5, an attempt has been made to correlate the PMR enol proton resonance shifts with the infrared chelate carbonyl absorption frequencies. Although the number of measurements is limited, the general tendency is clear: a large negative enol proton PMR shift is accompanied by a low chelate carbonyl absorption frequency. This indicates a very strong interaction between the enol proton and the carbonyl group and may be taken as a proof that the assignment of the chelate carbonyl absorption is justified. The same conclusion can be drawn qualitatively from a study of the hydroxyl stretching absorption but, unfortunately, these bands are too weak for a quantitative study. Deuteration experiments have been started in order to investigate other hydroxyl absorptions. It has already been found that the rate of hydrogen exchange between acetyldimedone and heavy water is very low. This is in marked contrast to the behaviour of simple β-diketones, *e.g.* acetylacetone, and is an additional indication of the very strong intramolecular hydrogen bonding present.

In a discussion of the enolisation and acidity of carbonyl compounds, Hammond [19] points out that the formation of intramolecular hydrogen bonds and the separation in space of the oxygen atoms are important factors influencing the enolisation of β-dicarbonyl compounds. The first factor is well known and the second is exemplified by the pronounced enolisation of *trans*-fixed β-diketones which cannot form intramolecular hydrogen bonds although the enols may sometimes be stabilised by dimerisation [10].

In β-diketones, these tendencies, however, may work in the same direction since *trans*-conjugation to the non-chelated carbonyl group is possible. That this conjugation is very strong indeed is indicated by the infrared absorption of the non-chelated carbonyl group [3], which occurs at approximately the same frequency as that in dimedone methyl ether [18]. This conjugation effect has also been discussed by Schwarzenbach and Lutz in connection with the acidity of triacetylmethane [11].

The differences between the two unconjugated β-triketones, triacetylmethane and acetyldimedone, are to be expected by analogy with the well-known tendency of cyclic ketones to enolise more readily than the acyclic analogues [19].

The pronounced influence of external conjugation on the properties of the conjugated chelate system could be ascribed in part to steric factors but further experimental material is required for a discussion.

As far as the structure of ceroptene and the choice between structures IV and V for the O-methyl-3-acylfilicinic acids are concerned, the splitting found in the PMR spectra indicates that two enolic species are present in the solutions. The rate of interconversion is apparently low and the equilibrium proportions are dependent on the solvent. As calculated from the relative intensities of the split signals, the equilibrium constants are mostly of the order of 3—8 which means a free energy change of less than 1 kcal/mole. The tautomeric forms must therefore be very similar and the hydrogen bonds should be of approximately the same strength. Since only structure IV permits the existence of two tautomeric enols with intramolecular hydrogen bonds of similar properties (IV b and c), the results strongly indicate that ceroptene is actually 5-methoxy-2-cinnamoyl-6,6-dimethyl*cyclo*hex-4-ene-1,3-dione (IV, R = Ph—CH=CH—). Other structures, such as 5-methoxy-4-cinnamoyl-6,6-dimethyl-*cyclo*hex-4-ene-1,3-dione, which have not been discussed above, are ruled out by these considerations.

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