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THE STRUCTURE OF THUJIC ACID:
7,7 DIMETHYLCYCLOHEPTATRIENE-3-CARBOXYLIC ACID

R.E. Davis[1] and A. Tulinsky

Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

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FOR years, three structures have been considered for tropilidene: the norcaradiene, the planar cycloheptatriene and the non-planar cycloheptatriene.[2,3,4] For the resolution of this problem, thujic acid, as an appropriate derivative, seemed particularly suitable for an X-ray crystallographic structure determination. Chemical studies on thujic acid itself suggest a cycloheptatriene type system, but these studies are by no means unequivocal.[5] However, N.M.R. does support such a system.[3,6] The N.M.R. spectra of thujic acid methyl ester and its p-bromophenacyl ester are shown in Figs. 1(a) and (b).[7] In Fig. 1(a), the two peaks near 2.2 τ are due to the hydrogens α to the carboxyl group, peaks in the region of 3.2-4.9 τ are the ethylenic hydrogens of thujic acid, the peak at 6.2 τ is the ester methyl while the one at 8.9 τ is due to the gem-dimethyl hydrogens. Thus, there is no evidence for tertiary bridge hydrogens of a norcaradiene type

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[1] NIH Predoctoral Fellow, 1961-62.

[2] E.J. Corey, H.J. Burke and W.A. Remers, J. Amer. Chem. Soc. 77, 4941 (1955).

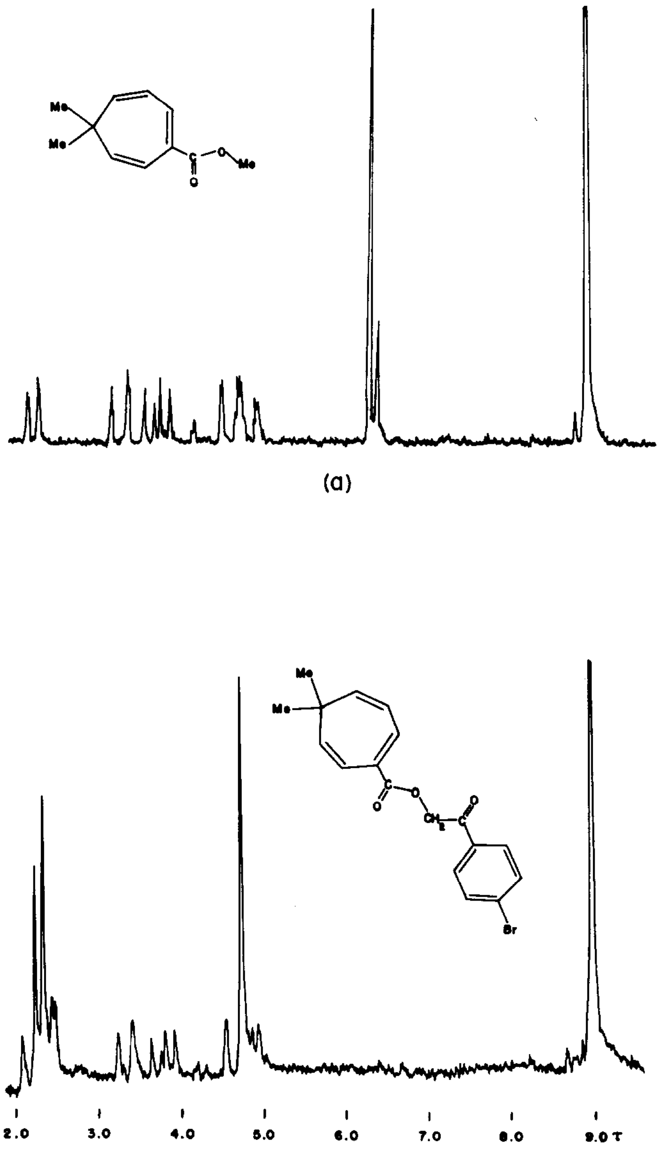
[3] W. von E. Doering, G. Laber, R. Vonderwahl, N.F. Chamberlain and R.B. Williams, J. Amer. Chem. Soc. 78, 5448 (1956).

[4] M.V. Evans and R.C. Lord, J. Amer. Chem. Soc. 82, 876 (1960).

[5] J. Gripenberg, Acta Chem. Scand. 5, 995 (1951).

[6] J. Gripenberg, Acta Chem. Scand. 10, 487 (1956).

[7] We should like to thank Dr. M.R. Willcott for measuring these spectra.



(a)

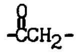
(b)

FIG. 1

system. In Fig. 1(b) the ester methyl disappears and a peak occurs at 4.8 τ corresponding to the aliphatic hydrogens of the phenacyl. The group of peaks in the region of 2.1-2.4 τ are due to the vinyl hydrogens of the phenyl and the α hydrogens of thujic acid.

Now, the most striking feature of both of these spectra is that the gem-dimethyl groups seem to be equivalent. This can be accounted for by a planar, pseudo-aromatic system[3,4] or by a non-planar one that is undergoing an inversion so that its time-averaged structure appears to be planar to N.M.R. This X-ray structure determination was undertaken to distinguish between the following alternatives: (1) planar and pseudo-aromatic, (2) a norcaradiene type structure, (3) a non-planar C_7 with 1,6 overlap or possibly, (4) an even more non-planar system.

The structure of thujic acid has been solved as its p-bromophenacyl ester employing three dimensional single crystal X-ray crystallographic techniques. Suitable single crystals were grown by slow evaporation of isopropanol. The crystals proved to be orthorhombic, space group Pbca, $\underline{a}$ = 6.29 Å, $\underline{b}$ = 30.50 Å, $\underline{c}$ = 17.10 Å, with 8 molecules/unit cell. Intensity measurements were made using counter techniques employing balanced filters and of the 2056 reflections accessible to 0.88 Å resolution, 1706 (83 per cent) were taken to be observable.

The structure was solved by the heavy atom method. The bromine atom positions were determined by considering the three Harker sections at $\underline{x} = 1/2$, $\underline{y} = 1/2$ and $\underline{z} = 1/2$. In order to enhance the bromine-bromine vectors, the Patterson coefficients were sharpened with $(\underline{z}_{\underline{Br}}/\underline{f}_{\underline{Br}})^2$, where $\underline{z}_{\underline{Br}}$ and $\underline{f}_{\underline{Br}}$ are bromine's atomic number and scattering form factor, respectively. A structure factor computation was then carried out based on these positions and bromine signs were assigned to the observed structure amplitudes, but only when the bromine structure factor exceeded 0.1 of its maximum possible contribution. A three dimensional electron density was computed with this set of phases, the series including 1258 coefficients. Of the 23 peaks in this density ranging from 2.1 e Å^{-3} to 4.5 e Å^{-3}, 21 belonged to the molecule and the other two were taken to be spurious; the latter were in unreasonable positions and were also the smallest two peaks. Although somewhat distorted, the phenyl group and the cycloheptatriene system were easily recognized as was the  $-\overset{O}{\overset{\|}{C}}CH_2-$ configuration of the phenacyl. The only uncertainties as to the complete structure were (1) the carboxylic acid function of thujic acid (the interatomic distances and bond angles in and around this region were particularly unreasonable) and (2) the unambiguous location of the *gem*-dimethyl groups, since the peaks in their expected vicinity were rather weak (2.3 and 2.8 e Å^{-3} respectively).

A structure factor computation was then carried out based on bromine plus 16 carbon atoms (omitting the above uncertainties). An electron density based on these phases revealed the carboxylic acid function clearly; all three peaks increased significantly in height and one unexpectedly large shift occurred (0.8 Å). The included atoms were confirmed as their heights increased by a factor of two or more and their shapes became much more conventional. The only real uncertainty was the location of one of the methyl groups. The larger one returned at about its original peak height whereas the other one decreased to 2.0 e Å^{-3}. Therefore, it was omitted from the next structure factor computation which included bromine plus 20 carbon atoms. Since the previous cycle indicated that the absolute scale was high by about a factor of two, the observed data were rescaled and the *R* factor for this computation turned out to be 0.35. In order to obtain more quantitative shifts in atomic coordinates and to be able to approximate individual thermal parameters and to be able to fix the forementioned methyl group with a higher degree of confidence, both an electron and a difference density were computed at this stage. The methyl group omitted from the structure factor computation appeared as 3.4 e Å^{-3} in the electron and as +3.3 e Å^{-3} in the difference density, thus removing all doubt as to its identity.

Refinement of atomic parameters of bromine plus 21 atoms of correct chemical identity proceeded from here through several cycles of electron and difference density considerations. Then the method of least squares refinement was adopted, first simply on atomic coordinates and individual isotropic thermal parameters and then converting to individual anisotropic thermal parameters. In addition, on several occasions, the least squares refinement was interrupted with difference density intervention. The *R* factor presently stands at 0.098 and the electron density determined by this set of phases is shown in Fig. 2.

In the crystal, the molecules are stretched out along the long *b* axis and the structure is unusual in that its planar or nearly planar portions lie approximately parallel rather than the more common way, perpendicular to the short axis. The cycloheptatriene ring tends to show alternate partial single and nearly true double bond character, typical of a conjugated but not of an aromatic system (Fig. 3); furthermore, the C_1-C_6 distance (2.41 Å) definitely precludes a norcaradiene structure. Moreover, the ring is markedly non-planar. The 1,2,5 and 6 carbon atoms are coplanar to within ±0.01 Å; the 7 carbon is 0.63 Å out of this plane while the 3 and 4 carbon atoms are non-planar by 0.48 and 0.48 Å, respectively, and the molecule assumes a boat configuration. Somewhat similar observations have been made on cycloheptatriene-molybdenum-tricarbonyl ($C_7H_8Mo(CO)_3$); however, here, six of the atoms are very nearly planar while the C_7 is not by 0.67 Å.[8] The most interesting feature of all about thujic acid is that its structural configuration permits the possibility of having the lobes of the *p*-electrons of C_1 and C_6 to overlap to some extent, but *only* below and not above the

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[8] J.D. Dunitz and P. Pauling, *Helv. Chim. Acta* *43*, 2188 (1960).

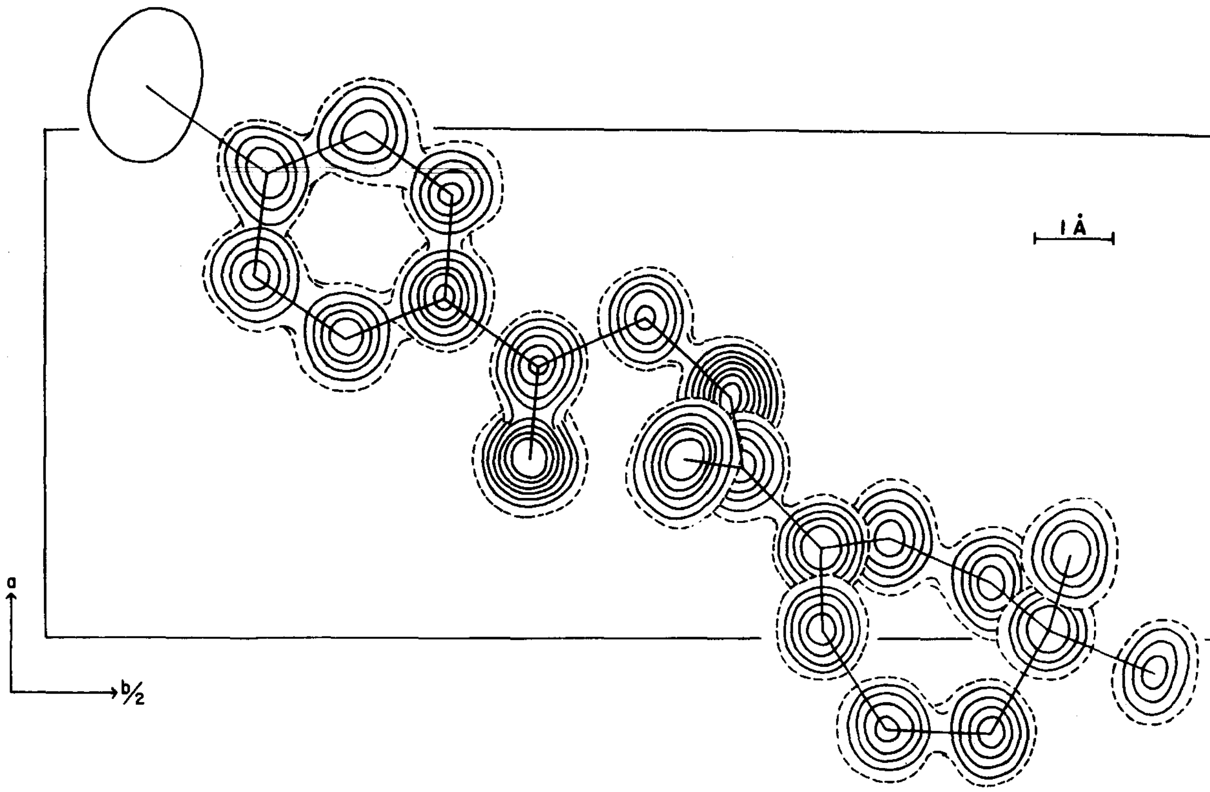

FIG. 2. Composite electron density of the p-bromophenacyl ester of thujic acid viewed along c; contours are at 1 e Å^{-3}, 1 e Å^{-3} broken.

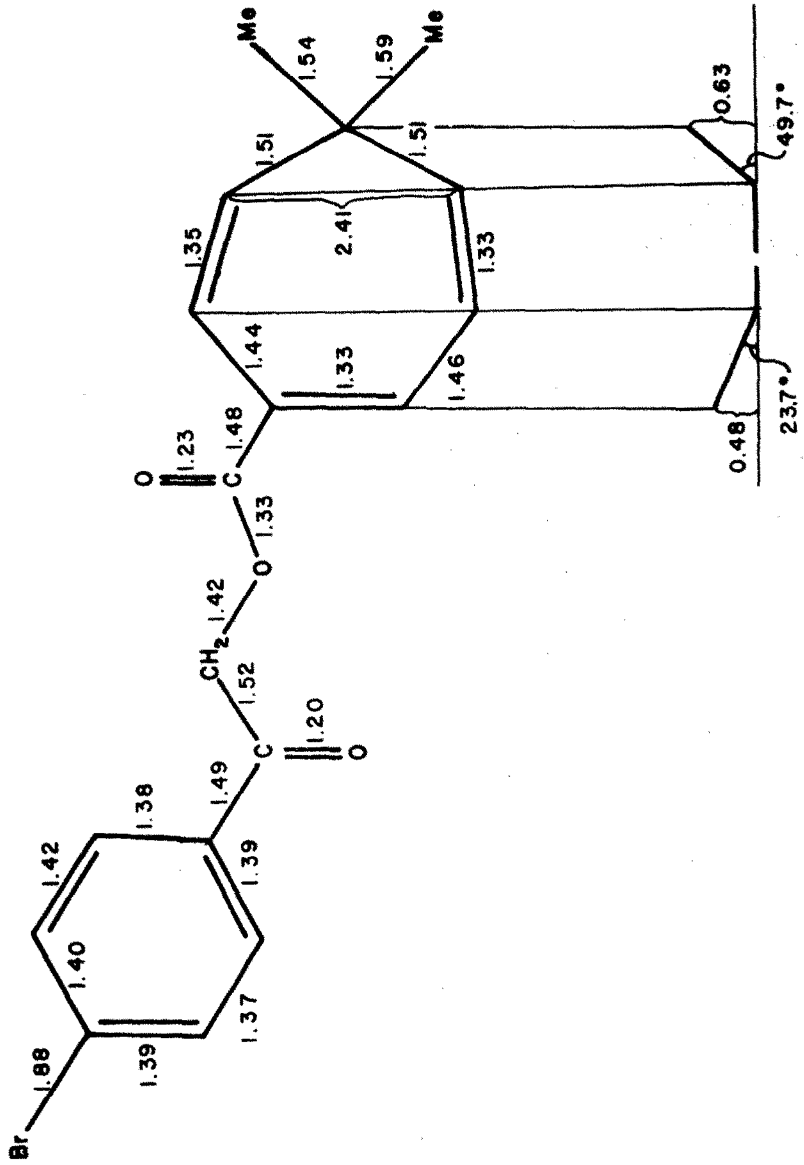
Me
1.54
Me
1.59
1.51
1.51
1.35
2.41
1.33
1.44
1.33
1.46
1.48
O
1.23
C
1.33
O
1.42
CH2
1.52
C
1.20
O
1.49
1.38
1.42
1.39
1.40
1.37
1.39
1.88
Br
0.63
49.7°
23.7°
0.48

FIG. 3

boat, thus giving rise to a kind of a "half π bond", its exact nature depending on the amount of overlap. Therefore, the π-electron bonding system in this molecule resembles "half of a non-planar benzene" below, and "half of a hexatriene" above, the boat. Doubtless, somewhat similar situations must exist in other compounds, where partial bonding has been thought to take place. And finally, the 7 carbon atom is undergoing an abnormally large vibration, as is evidenced by its and the gem-dimethyl peak heights, and, also, their large thermal parameters. This is consistent with the C_7, the C_3 and the C_4 atoms of thujic acid undergoing a relatively rapid inversion in solution; in the solid, however, with crystal field forces to contend with in addition to satisfying space requirements, such an inversion is most likely inhibited to a great extent.

A number of the hydrogen atoms have already been located and refinement is still in progress in order to locate the rest of them. The positions of the thujic acid hydrogens are of importance in that they may furnish some additional useful information about its novel π-electron bonding system.

A detailed account of this structure determination will appear elsewhere.

We should like to thank Professor W. von E. Doering for suggesting this problem and Dr. Wolfgang Kirmse for preparing the phenacyl ester.

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