*Infra-red Spectra of Natural Products. Part II.** *Compounds containing the* cyclo*Propane Ring.*

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The infra-red spectra of a number of steroid and terpenoid compounds containing the *cyclo*propane ring have been measured. The C–H stretching absorption at 3040—3058 cm.$^{-1}$, found when the three-membered ring contains a CH_2 group, confirms that the C–H bonds of the ring are very similar to the sp^2 type in ethylene. This information is useful in the identification of *cyclo*propane rings in unknown compounds.

Some of the chemical properties of *cyclo*propane show that it resembles unsaturated compounds rather than the larger saturated rings. For instance, it gives addition products with bromine (1 : 3-dibromopropane) and with hydrogen bromide (*n*-propyl bromide) whereas the larger-ring homologues give substitution products if they react at all. Therefore it is probable that in electronic structure a *cyclo*propane ring is somewhat similar to the ethylenic double bond, and this is reflected in its spectroscopic properties. Walsh (*Trans. Faraday Soc.*, 1949, **45**, 179) has summarised the results of ultra-violet measurements on *cyclo*propane itself and on compounds in which the three-membered ring is " conjugated " with an ethylenic double bond or a carbonyl group. In all these the absorption is more intense and at a longer wave-length than might be expected, indicating that the ring has a system of weakly bound electrons similar in behaviour to the π electrons of ethylene.

Structural Considerations.—Electron-diffraction measurements on *cyclo*propane (Bastiansen and Hassel, *Tids. Kjemi Berg. Met.*, 1946, **6**, 71) show that the H–C–H angle is $118{\cdot}2° \pm 2°$. This is significant, since it is almost the same as that found in ethylene, and indicates that the carbon valencies towards hydrogen are close to the sp^2 hybrid type characteristic of ethylenic carbon atoms. Theoretical arguments supporting this hypothesis have been advanced by Coulson and Moffit (*Phil. Mag.*, 1949, **40**, 1) and by Walsh (*loc. cit.*). These theoretical studies also indicate that the electrons binding the carbon atoms together behave in certain ways like the electrons in the C=C bond of ethylene.

Infra-red Spectra.—In the infra-red spectrum there are two regions in which information may be obtained about the properties of the *cyclo*propane ring. First, the conjugating effect of the three-membered ring with a carbonyl group, which results in a lowering of carbonyl frequency, has been observed by Josien and Fuson (*Compt. rend.*, 1950, **231**, 1511) for 3 : 5-*cyclo*cholestan-6-one (I; C=O frequency 1690 cm.$^{-1}$) and by Jones, Humphries, Herling, and Dobriner (*J. Amer. Chem. Soc.*, 1952, **74**, 2821) for a 16 : 17-methylene-20-ketosteroid (II; C=O frequency 1685 cm.$^{-1}$).

Secondly, the region of C–H stretching absorption should show whether the C–H bonds of the *cyclo*propane ring are of the sp^2 hybrid type or not, since it is known that ethylenic C–H bonds have a considerably higher vibration frequency than have the tetrahedral type (Fox and Martin, *Proc. Roy. Soc.*, 1940, *A*, **175**, 208). It is with this region that this paper is mostly concerned. A preliminary account of this work (Cole, *Chem. and Ind.*, 1953, 946) has already been published.

Josien (*Compt. rend.*, 1950, **231**, 131) reported that in the infra-red spectra of a series of 3 : 5-*cyclo*steroids, a " point of inflexion " was observed at $3{\cdot}30\ \mu$ (3030 cm.$^{-1}$), and it was suggested that this unresolved band was related to a vibration of a CH-group adjacent to the *cyclo*propane ring. Those measurements were carried out by using a lithium fluoride prism which is capable of high resolving power, and in view of the results reported below it is surprising that the band was not more completely resolved from the rest of the C–H absorption.

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* Part I, *J.*, 1952, 4969.

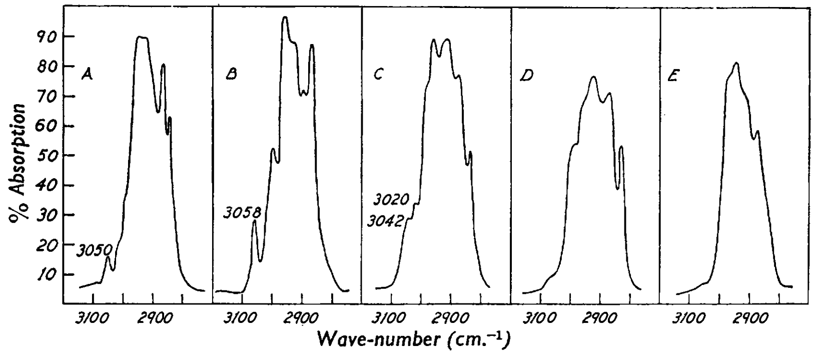
EXPERIMENTAL

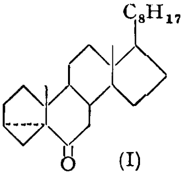
The infra-red spectra were measured on a Grubb-Parsons spectrometer, Model S3A, equipped with a Perkin-Elmer thermocouple, chopper and rectifier assembly, and No. 81 amplifier. Prisms of calcium fluoride (3—8 μ) and sodium chloride (8—14 μ) were employed, the latter in the double-pass system which has been previously described (Cole, *J. Opt. Soc. Amer.*, 1953, **43**, 807). The compounds were studied in carbon tetrachloride for the region 3—8 μ and in carbon disulphide for 8—14 μ, and cells of 1·3 mm. and 3 mm. were employed.

RESULTS AND DISCUSSION

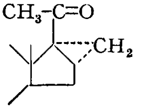
The C–H stretching region of the spectra of 3 : 5-*cyclo*cholestane (*i*-cholestane; III; *A*), thujane (IV; *B*), α-thujene (V; *C*), car-3-ene (VI; *D*) and lanosta-8 : 24-dienyl acetate (VII; *E*) * are shown in Fig. 1. The first three of these compounds have a CH_2 group included in the *cyclo*propane ring, the fourth is substituted at all carbons of the three-membered ring, and the last has no *cyclo*propane ring. It will be noticed that the band at 3024—3058 cm.$^{-1}$ only appears when there is a CH_2 group included in the *cyclo*propane ring, and must be due to a vibration of this particular CH_2 group. The high frequency of this absorption confirms the earlier suggestion from ultra-violet and electron-diffraction results that these C–H bonds are of sp^2 type.

FIG. 1. *Infra-red spectra in the* C–H *stretching region.* (CCl_4 *solutions*; CaF_2 *prism.*)





(I)



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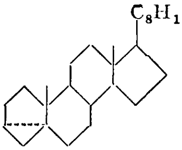

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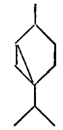
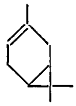
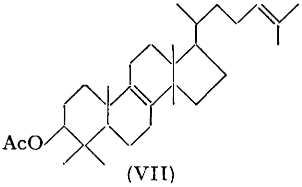


(IV)

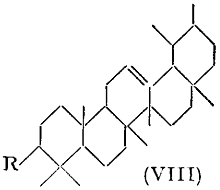
(V)



(VI)



(VII)



(VIII)

CH groups attached to double bonds in steroids and similar compounds have stretching vibrations in the range 3015—3075 cm.$^{-1}$ (Jones, Williams, Whalen, and Dobriner, *J. Amer. Chem. Soc.*, 1948, **70**, 2024; Jones, Humphries, Packard, and Dobriner, *J. Amer. Chem. Soc.*, 1950, **72**, 86; Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 2402). Some of the spectra in Fig. 1 exhibit this absorption, *e.g.*, α-thujene at 3020 cm.$^{-1}$, but this should not be confused with the more pronounced absorption at a higher frequency due to the

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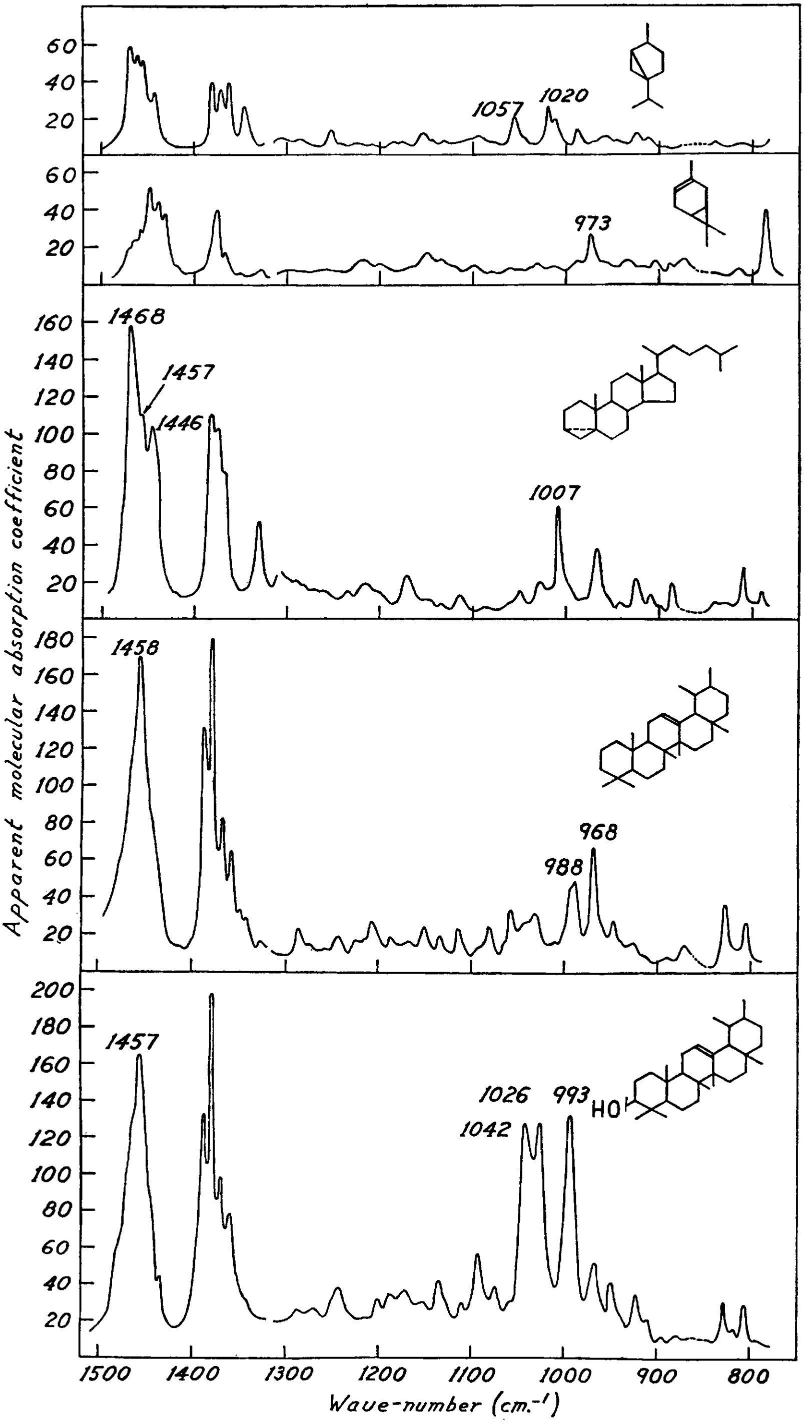
* Numbered according to standard steroid rules.

FIG. 2. *Infra-red spectra in the range* 750—1500 *cm.*$^{-1}$. *The dotted region near* 850 *cm.*$^{-1}$ *is uncertain because of* CS_2 *absorption. The slight break in the curves between* 1300 *and* 1350 *cm.*$^{-1}$ *indicates the change from* CCl_4 *solvent*-CaF_2 *prism to* CS_2 *solvent*-NaCl *prism.*



CH_2 group of the *cyclo*propane ring. The latter should be helpful in the identification of three-membered rings in certain types of unknown compounds.

Measurements at Longer Wave-lengths.—Derfer, Pickett, and Boord (*J. Amer. Chem. Soc.*, 1949, **71**, 2482) have suggested that a band near 9·9 μ (1010 cm.$^{-1}$) can be used to identify the *cyclo*propane ring. The spectra of a number of compounds in the range 1500—780 cm.$^{-1}$ are shown in Fig. 2. These spectra are plotted by using the apparent molecular absorption coefficient (Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72) and allow one to compare more accurately than otherwise the relative intensities of absorption bands from one spectrum to another. α-Amyrene (VIII; R = H) and α-amyrin (VIII; R = OH) are included in Fig. 2 to facilitate comparison with a hydrocarbon which does not contain the *cyclo*propane ring and with a hydroxy-compound respectively.

It will be noticed that the hydrocarbons containing the *cyclo*propane ring do sometimes exhibit bands of medium intensity near 1010 cm.$^{-1}$. However, compounds containing hydroxyl (or ester) groups have much greater absorption in this region and it is obviously impossible to use this method of identifying *cyclo*propane rings in the presence of oxygen-containing substituents. The case of car-3-ene would also be uncertain since its strongest peak near 1010 cm.$^{-1}$ is at 973 cm.$^{-1}$, at which point α-amyrene also absorbs fairly strongly. It is possible that only those compounds in which the *cyclo*propane ring is not fully substituted exhibit the stronger absorption near 1010 cm.$^{-1}$, although Derfer *et al.* (*loc. cit.*) suggest that it is not limited to those compounds. Reid (*Chem. and Ind.*, 1953, 846) has criticised similar suggestions by Derfer *et al.* (*loc. cit.*) regarding the identification of *cyclo*butane rings.

The spectra of the above compounds have also been studied in the region of C–H bending vibrations near 1350—1480 cm.$^{-1}$ (Jones and Cole, *J. Amer. Chem. Soc.*, 1952, **74**, 5648) but no absorption which can be specifically related to the presence of the *cyclo*propane ring was found.

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