*Infra-red Spectra of Natural Products. Part III.** cyclo*Artenol and Phyllanthol.*

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The infra-red spectra of *cyclo*artenol and phyllanthol show that these compounds have an unsubstituted CH_2 group included in their *cyclo*propane rings. This information considerably reduces the number of possible formulæ for each compound. The C–H bending region of the infra-red spectrum can be used to characterise the ring systems of new triterpenoids.

(1) cyclo*Artenol.*—Barton (*J.*, 1951, 1444) established the presence of an *iso*propylidene group in the side-chain, and of a *cyclo*propane ring, in *cyclo*artenol. These observations were confirmed by Bentley, Henry, Irvine, and Spring (*Chem. and Ind.*, 1953, 217; *J.*, 1953, 3673) who also isolated lanost-9(11)-enyl acetate (I) from the reaction of *cyclo*artanyl acetate with hydrogen chloride.

Spring and his collaborators showed that their results are most easily interpreted if the *cyclo*propane ring in *cyclo*artenol extends from $C_{(9)}$, and this allows the five possible structures (II)—(VI).†

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* Part II, preceding paper.

† The author is indebted to Professor D. H. R. Barton and to Professor F. S. Spring who independently pointed out the possibility of structure (VI), after publication of a preliminary note (Cole, *Chem. and Ind.*, 1953, 946).

It has been shown in Part II * that a CH_2 group in a three-membered ring is responsible for an infra-red absorption band near 3045 cm.$^{-1}$, and this band is present in the spectra of all the *cyclo*artenol derivatives which have been studied (see Fig. 1 and the Table).

Frequency of " cyclo*propyl* CH_2 *" absorption in* cyclo*artenol and phyllanthol derivatives (cm.*$^{-1}$; CCl_4 *solution).*

*cyclo*artenol	3042	*cyclo*artanol	3042	phyllanthol	3055
*cyclo*artenone	3038	*cyclo*artenyl acetate	3036	phyllanthane	3055
*cyclo*artene	3037	*cyclo*artanyl acetate	3037	phyllanthone	3055
*cyclo*artane	3040			phyllanthyl acetate	3052

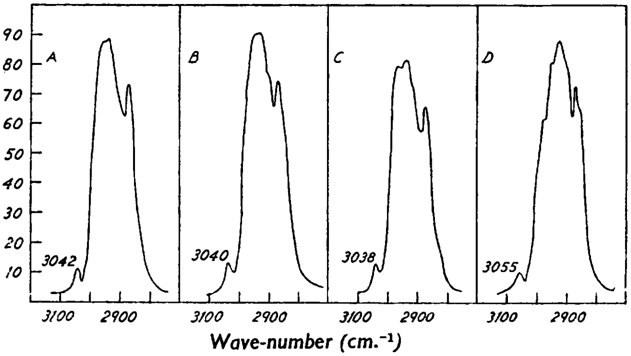
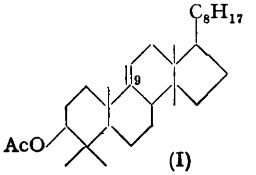


FIG. 1. *Infra-red spectra in the* C–H *stretching region* (CCl_4 *solutions*; CaF_2 *prism*).

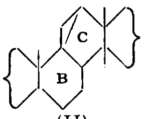
A, *cyclo*artanol
B, *cyclo*artane
C, *cyclo*artenone
D, phyllanthane

Structures (III), (IV), and (V) are therefore eliminated but the results of the present work do not distinguish between (II) and (VI).

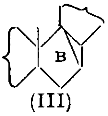
After this work was completed Barton, Warnhoff, and Page (*Chem. and Ind.*, 1954, 220) used other infra-red measurements to show that (VI) is the correct structure, while Henry and Spring (*Chem. and Ind.*, 1954, 189) supported this result by eliminating (II).



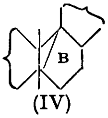
(I)



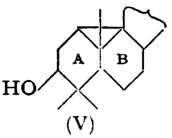
(II)



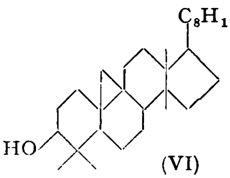
(III)



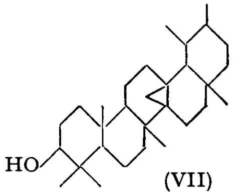
(IV)



(V)



(VI)



(VII)

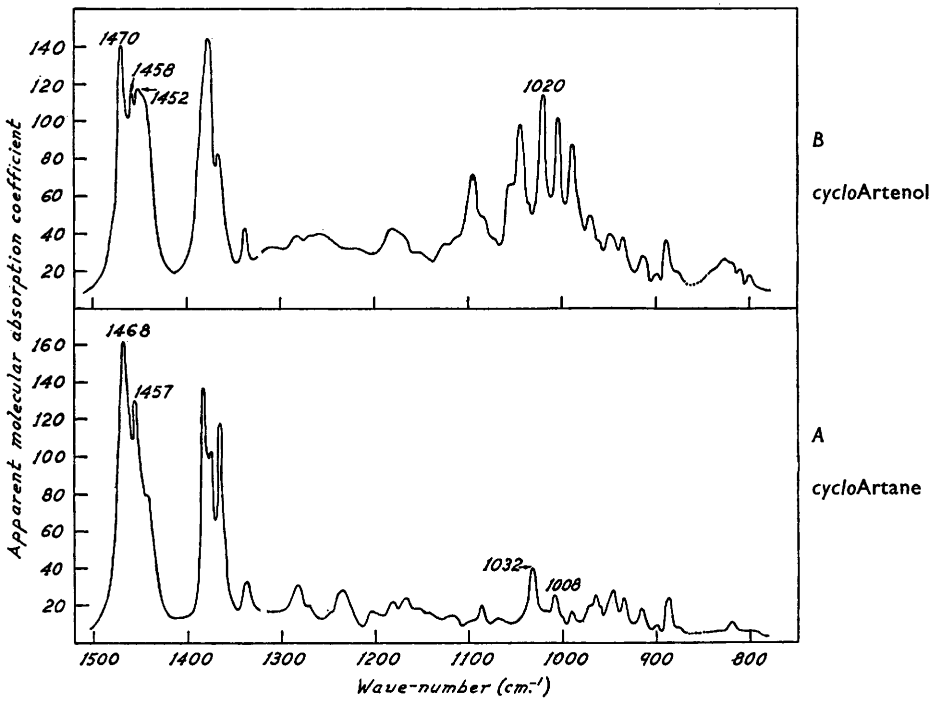
Consideration has been given in Part II * to the infra-red band near 1010 cm.$^{-1}$, suggested by Derfer, Pickett, and Boord (*J. Amer. Chem. Soc.*, 1949, **71**, 2482) to be characteristic of the *cyclo*propane ring, and it is possible that the band at 1032 cm.$^{-1}$ in the spectrum of *cyclo*artane (Fig. 2*A*) is due to this ring. However, as pointed out previously, it is extremely unwise to try to use the absorption in this region as an indication of the presence of a *cyclo*propane ring if the compound has an oxygen-containing substituent (see Fig. 2*B*).

(2) *Phyllanthol.*—Measurements in the C–H stretching region have been carried out on phyllanthol (Barton and de Mayo, *J.*, 1953, 2178) and a number of its derivatives, and the presence of the absorption band at 3052—3055 cm.$^{-1}$ (Fig. 1 and the Table) indicate that this compound also contains a CH_2 group within its three-membered ring. Later work by

Barton, Warnhoff, and Page (*loc. cit.*; *J.*, 1954, 2715) has shown that phyllanthol is represented by (VII) which agrees with the above finding.

(3) *Infra-red Absorption and the Carbon Skeleton of Triterpenoids.*—In general, most of the specific infra-red absorption bands are related to substituent groups rather than to the carbon skeleton of a triterpenoid. It would be useful in the early stages of an investigation to be able to tell whether a new compound belonged to the tetracyclic or pentacyclic series, and, if possible, to be able to distinguish between the different classes within these series. It appears that the C–H bending region of the spectrum (1350—1480 cm.$^{-1}$) will allow such a distinction to be made, at least between the tetra- and penta-cyclic types. To obtain the maximum amount of information, this region should be studied by using a calcium fluoride prism and solutions in carbon tetrachloride.

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.*



It has been shown that in the spectra of steroids (Jones and Cole, *J. Amer. Chem. Soc.*, 1952, **74**, 5648) the bending frequency associated with five- and six-membered ring methylene groups occurs near 1450—1455 cm.$^{-1}$, while that of side-chain methylene groups lies near 1470 cm.$^{-1}$. These frequencies are indicated for *cyclo*artane and *cyclo*artenol in Fig. 2 and should be compared with those marked in Fig. 2 of the preceding paper for 3 : 5-*cyclo*-cholestane, and α-amyrene and α-amyrin. By this means it seems that the type of triterpenoid skeleton can be identified. Further work along these lines continues.

Experimental.—The experimental details were as described in the preceding paper.

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