Terpenoids XLII. 8-Substituted Tricyclenes

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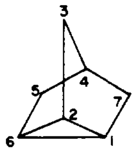
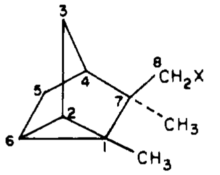
Two infrared bands near 876 and 822 cm.$^{-1}$, respectively have been found to be characteristic of 8-substituted tricyclene system. The previously reported frequency assignments for some nortricyclene and tricyclene derivatives near 3050 and 854 cm.$^{-1}$ have been confirmed for fifteen 8-substituted tricyclene derivatives.

THE α-SANTALENE SERIES constitutes a group of compounds containing the tricyclene skeleton in which the 8-position has an aliphatic side-chain as substituent. The relative paucity of adequate spectral data of tricyclene derivatives in literature coupled with the availability of a good number of such compounds at our disposal prompted us to examine their infrared spectra for some possible correlation.

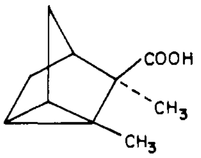
It is known (*2, 3, 10, 11, 13, 14, 18*) that the cyclopropyl ring structure in organic compounds can be identified by characteristic absorption bands in the regions near 3050, 1020, and 866 cm.$^{-1}$, though the reliability of these assignments have been questioned (*1, 8, 12*). Two bands near 3050 and 802 cm.$^{-1}$ have been considered characteristic of nortricyclene system (I) (*14*). Nortricyclene itself does not absorb at 854 cm.$^{-1}$ (*14*), but 1-substituted nortricyclenes (*7, 9, 13, 14, 19*) are reported to absorb near 854 and 788 cm.$^{-1}$. Nortricyclenes having a substituent at the 3-position were found to absorb in the region 800–806 cm.$^{-1}$ (*17*); a doublet between 800–818 cm.$^{-1}$ (*14*) was reported as characteristic of such system. Some tricyclene derivatives (*4*) showed a band at 858 cm.$^{-1}$ while certain 1-substituted tricyclenes (*6*) absorbed in the regions 3076–3100 and 840–854 cm.$^{-1}$. Absorptions of nortricyclene compounds in the near infrared regions (*5*) have also been reported recently.



I



II



III

During our investigations in the santalene series (*15, 16*) we have examined the infrared spectra of several tricyclene derivatives, substituted at the 8-position by various functional groups. The compounds studied include hydrocarbons, alcohol, ketone, acid, ester, and epoxide. The absorption in four characteristic infrared regions of fifteen compounds in this series are summarized in Table I. From a detailed examination of the spectra, four prominent and well-defined bands near 3050, 876, 854, and 822 cm.$^{-1}$, respectively, are found to be quite characteristic of 8-substituted tricyclene system (II). The bands at 876 and 822 cm.$^{-1}$ have not been reported previously. These four bands, together could be employed for the identification of the tricyclene system and the position of the substituents present.

The region 3050–3100 cm.$^{-1}$ A sharp band or shoulder was observed in the region 3050–3100 cm.$^{-1}$ in all the compounds listed in Table I and may be considered as an evidence for the C–H stretching of the hydrogen atoms attached to the cyclopropane ring system. This band is of considerable value in the diagnosis of cyclopropane ring in saturated compounds of the tricyclene series in which the interfering group (C–C double bond) is absent.

The region 1010–1020 cm.$^{-1}$ The hydrocarbons tricyclene, α-santalene and dihydro α-santalene show weak absorption in this region, which is not prominent enough to be assigned to the cyclopropane ring. In the case of oxygenated compounds, the bands in this region are masked by the absorption due to the functional groups and are therefore unreliable for the identification of tricyclene ring system.

The region 870–878 cm.$^{-1}$ A sharp band at 876 cm.$^{-1}$ appears to be characteristic of 8-substituted tricyclenes. Significant absorptions appear consistently in the region 870–878 cm.$^{-1}$, with the majority centered near 876 cm.$^{-1}$, as shown in Table I. The only possible interfering group in this region is the exocyclic methylene bond. However, the band at 876 cm.$^{-1}$ is prominent even in the presence of a $>C=CH_2$ bond in an aliphatic chain as found in the case of 2-isopropenyl 3 (8)-tricyclyl propanol (Table I).

A deviation is noted in the case of teresantalic acid (III) which absorbs on the higher frequency side. This may probably be due to the absence of $-CH_2-$ group on the substituent ($-COOH$) at C (7).

The region 820–860 cm.$^{-1}$ All the compounds listed in Table I show a strong band at 854 cm.$^{-1}$ and a band at 822 cm.$^{-1}$ of medium intensity. An interfering functional group absorbing in the neighborhood (790–840 cm.$^{-1}$) of the band at 822 cm.$^{-1}$ is the trisubstituted double bond. The shape of the curve in the region 800–880 cm.$^{-1}$ is almost the same (Figure 1) (an intense band at 854 cm.$^{-1}$,

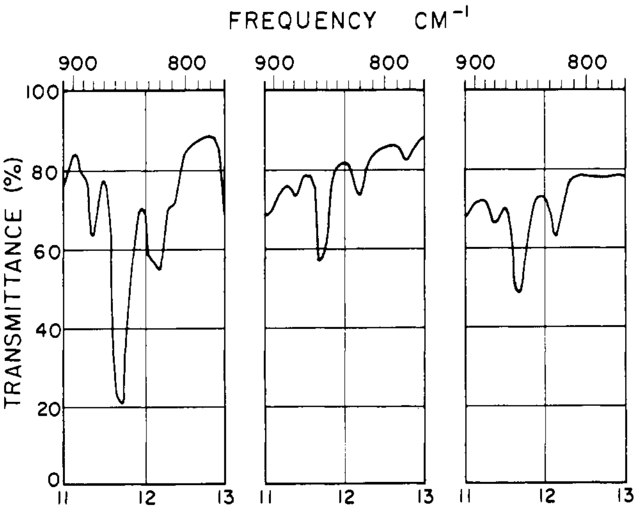


Figure 1. Infrared spectra of 8-substituted tricyclenes

A. Dihydro α-santalene (liquid cell, 0.05 mm.)
B. Tricycloekasantalic acid (in Nujol)
C. 2-Homo-8-tricyclyl 3-keto butanol (liquid film)

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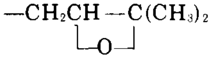
Table I. Characteristic Absorptions of 8-Substituted Tricyclene System

		Frequency, Cm.$^{-1}$			
Compound	Substituent, X	~3050	~876	~854	~822
Tricyclene	$-H$	3069	873	856	818
α-Santalene	$-CH_2CH=C(CH_3)_2$	3086	879	855	823
Dihydro α-santalene	$-CH_2CH_2CH(CH_3)_2$	3077	880	858	822
α-Santalol	$-CH_2CH=C(CH_3)CH_2OH$	3110	877	852	823
Dihydro α-santalol	$-CH_2CH_2CH(CH_3)CH_2OH$	3110	877	852	823
Tricycloekasantalol	$-CH_2CH_2OH$	3100	872	853	820
Tricycloekasantalic acid	$-CH_2COOH$	3058	877	853	821
Tricycloekasantalic acid methyl ester	$-CH_2COOCH_3$	3058	875	852	820
2-Isopropenyl 3(8)-tricyclyl propanol	$-CH_2CH(CH_2OH)C(=CH_2)CH_3$	3140	874	854	821
2-Isopropyl 3(8)-tricyclyl propanol	$-CH_2CH(CH_2OH)CH(CH_3)_2$	3067	877	854	820
2-Homo 8-tricyclyl 3-keto butanol	$-CH_2CH(CH_2OH)COCH_3$	3096	878	856	824
Teresantalol	$-OH$	3125	875	854	824
α-Santalal semicarbazone	$-CH_2CH=C(CH_3)CH=NNHCONH_2$	3100	878	855	821
α-Santalene epoxide	 $-CH_2CH-C(CH_3)_2$	3060	870	852	823
Teresantalic acid	III	3086	891	855	820

another of medium intensity near 822 cm.$^{-1}$ and a comparatively weaker band at 876 cm.$^{-1}$) and is characteristic of compounds of the 8-substituted tricyclene series in the absence of interfering groups.

The results of the present findings may be interpreted in the following way. The band at 854 cm.$^{-1}$ arises from the 1-substituted nortricyclene system and hence remains constant in all compounds of the tricyclene series and is independent of the position and nature of the other substituents present. Schleyer's observations (*9, 19*) on the correlation between the spectral bands and the substituents present in various positions in the 1-substituted (methyl) nortricyclene system may be extended by the present studies as follows: When the substituent at the 1-position is kept constant (methyl) and the substituents $-CH_3$ and $-CH_2X$ (X = H or any functional group) are introduced at C(7) of the nortricyclene skeleton, the bands near 3050 and 854 cm.$^{-1}$ remain unaltered, and in addition, two more peaks appear near 876 and 822 cm.$^{-1}$, respectively. When the substituents at C(7) are methyl and carboxyl groups as in teresantalic acid (III), the band at 822 cm.$^{-1}$ becomes intense and that at 876 cm.$^{-1}$ either disappears or shifts to the higher frequency side.

The band near 822 cm.$^{-1}$ reported here as characteristic of 8-substituted tricyclenes may perhaps be identical with the previously reported band at 800-806 (*14, 17*), 784-788 cm.$^{-1}$ (*7, 9, 19*) shifted to the higher frequency side on account of the presence of two substituents at C(7) of the nortricyclene skeleton. In such cases, this band may be useful in the identification of the position of substituents present in the nortricyclene skeleton.

EXPERIMENTAL

The infrared spectra were recorded on a Perkin-Elmer Infracord Model 137B Spectrophotometer equipped with sodium chloride prism by H. Gopinath. Solid compounds were taken as nujol mulls and liquid samples as liquid films. The details of the preparation and properties of the various compounds listed in Table I have been described elsewhere (*15, 16*).

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