USE OF THE RAMAN SPECTRA FOR DETERMINING TRI- AND TETRASUBSTITUTED C = C BONDS IN TERPENE COMPOUNDS

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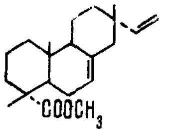
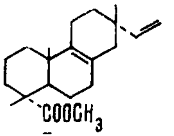
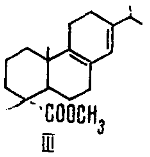
We have used the method of Raman spectroscopy [1-3] to detect tri- and tetrasubstituted bonds in methyl $\Delta^{7(8),15}$-isopimarate (I) and methyl $\Delta^{8(9),15}$-isopimarate (II), isolated in a study of the products of oxidation of isopimaric acid by molecular oxygen [4], and also in diterpenoids with other carbon skeletons – methyl palustrate (III) and cembrene (IV).



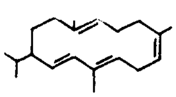
I



II



III



IV

In the IR spectra of compounds (I) and (II), which contain different types of double bonds, absorption bands are observed which correspond to bonds of the $R_1{-}HC{=}CH_2$ type (3080, 1640, 900 cm^{-1}) and the tri-

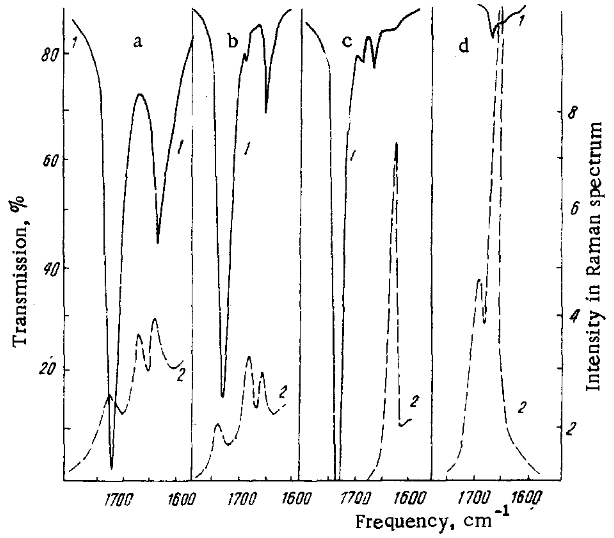


Fig. 1. IR and Raman spectra in the 1600-1800-cm^{-1} region of compounds (I) (a), (II) (IR spectrum in KBr, and Raman spectrum of a polycrystalline powder without solvent) (b), compound (III) (IR spectrum in CCl_4, c 10%, d 0.1 mm; Raman spectrum of the liquid) (c), and (IV) (IR spectrum in CCl_4, c 10%, d 0.1 mm; Raman spectrum in CCl_4, c 15%) d): 1) IR spectrum; 2) Raman spectrum.

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and tetrasubstituted bonds appear very feebly and cannot be identified (Fig. 1, curves a and b). This becomes particularly difficult if the molecule also contains a carbonyl or an ester group since they give strong absorption bands (at about 1700 cm^{-1}) which mask the already weak bands of the C=C bonds.

In contrast to the IR spectra, in the Raman spectra of compounds (I) and (II), in addition to the band at 1640-1650 cm^{-1} due to vibrations of a bond of $R_1-HC=CH_2$ type, a band also appears at 1673 cm^{-1} corresponding to the vibration of an isolated tri- or tetrasubstituted $-C=C-$ bond (see Fig. 1, curves a and b). This assignment is confirmed by the fact that in the Raman spectrum of methyl $\Delta^{8(9)}$-dihydroisopimarate there is a single bond in the 1600-1700-cm^{-1} range at 1671 cm^{-1}, and the 1640-1650-cm^{-1} band does not appear in either the IR or the Raman spectra.

The conjugation of the tri- and tetrasubstituted bonds in compounds (III) and (IV) leads to the appearance of very strong bonds in the Raman spectra at 1621 and 1650 cm^{-1}, respectively, which are due to the symmetrical stretching vibrations of the conjugated-bond system (see Fig. 1, curves c and d). The absorption bands in the IR spectra of (III) and (IV) in the 1600-1700-cm^{-1} region remain weak, as before, and cannot be used for identifying these bonds. The use of Raman spectroscopy enables the presence of tri- and tetrasubstituted double carbon bonds in the molecules of terpene compounds to be established.

The IR spectra were recorded on a Perkin Elmer 180 spectrophotometer, and the Raman spectra on a Coderg PH-1 spectrometer with a Spectra Physics 125 helium–neon laser ($\lambda = 6328$ Å) (an amount of substance of 20-40 mg is sufficient). The spectral widths of the inlet and outlet slits of the spectrometer were 8 cm^{-1}. Compound (II), with mp 69-70°C, $[\alpha]_D^{20}+90°$, was synthesized from methyl isopimarate (I) [5]. Cembrene (IV), with mp 56-58°C, $[\alpha]^{20}+208°$, was isolated from the oleoresin of the Siberian larch. Methyl palustrate (III) with n_D^{20} 1.5330, $[\alpha]_D^{20}+67°$, was obtained by the chromatography of the methyl esters of the resin acids of the oleoresin of the Scotch pine. The methyl $\Delta^{8(9)}$-dihydroisopimarate with n_D^{20} 1.5078, $[\alpha]^{20}+$ 55.2°, was obtained by the hydrogenation of (II).

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