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Infrared Spectra of Cinerolone and Synthetic *trans*-(2-Butenyl)-4-hydroxy-3-methyl-2-cyclopenten-1-one[1]

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The chrysanthemum acid esters of pyrethrolone and cinerolone constitute the principal insecticidal constituents of pyrethrum flowers. When cinerolone is reësterified with *d-trans*-chrysanthemum monocarboxylic acid, the resulting cinerin I has been shown to be of about the same order of toxicity as pyrethrin I, with the added advantage of greater stability.[2a] Recently Schechter, Green, and LaForge[3] have described the synthesis of a series of cyclopentenolones closely related to cinerolone, which, when esterified with synthetic or natural chrysanthemum monocarboxylic acids, yield esters having a high order of insecticidal activity, with knockdown and paralytic effects characteristic of pyrethrum extracts.

Schechter, Green and LaForge[3] thought it probable that their synthetic 2-(2-butenyl)-4-hydroxy-3-methyl-2-cyclopenten-1-one and natural cinerolone were *cis–trans* isomers, the synthetic compound being the *trans* form. Similar conclusions were reached by Harper[4] in the case of cinerone.[5] The *cis–trans* isomerism concerns the double bond in the butenyl side chain. The writer has found that the infrared absorption spectra of the two compounds are of value in differentiating them and in confirming their molecular structures.[6]

Experimental

Infrared spectra were obtained on a single-beam prism spectrometer equipped with a sodium chloride prism and sodium chloride windows and cells. Thermocouple output amplication is through a d. c. breaker-type amplifier, with zero adjustment at the amplifier. Blank and sample energy records were made consecutively, over limited spectral regions, on an electronic stripchart recorder. Within the ranges where solutions were used cell factors were applied to correct for differences in cell transmission by the solvent and solution cells. The effects of stray radiation were minimized by using shutters of LiF (15 to 9.9 microns), glass (9.9 to 5.4 microns), and opaque material (5.4 to 2.0 microns). Slit widths were changed stepwise, with actual slits of 1.070 mm. at 15 microns and 0.032 mm. at 2 microns. An automatically driven variable resistance (attenuator) served to maintain a fairly constant value of I_0 throughout the spectrum. The percentage transmission of the sample was determined on a point-to-point basis by dividing the intensity of radiation passing through the sample cell by the corresponding intensity passing through the blank cell.

Discussion of Results

The infrared spectra for wave lengths from 2 to 15 microns are presented in Fig. 1. From 2 microns to about 7.5 microns, in the higher frequency range where the bands are due exclusively to interatomic bonds, the two spectra are substantially the same. At higher wave lengths, where the absorptions are due in part to vibrations of the molecule as a whole, the spectra differ to a considerable degree. The most pronounced difference is at 10.36 microns, where the synthetic material alone has strong absorption. The natural material alone has an absorption band in the 14.0–14.6 micron region. The higher frequency bands have been correlated with the normal frequency ranges within which certain atomic groupings have been found to absorb, largely on the basis of the work of Barnes, Gore, Stafford and Williams.[7] The C=O band falls within the range assigned to α,β-unsaturated ketones (Cromwell, *et al.*,[8]). The correlations, presented in Table I, confirm important structural features of the molecule. In this table are included the lower frequency bands attributed to the *cis* and *trans* geometrical structures, as discussed below.

TABLE I

CORRELATION OF WAVE LENGTHS AND FUNCTIONAL GROUPS

Wave length in microns			
Cinerolone	Synthetic *trans*-	Frequency (cm.$^{-1}$)	Functional groups
2.91	2.91	3436	OH (bonded)
3.30	3.30	3030	Unsatd. C–H (aliphatic)
3.42	3.42	2924	Satd. CH_3; satd. C–H: satd. CH_2 (unresolved bands)
5.89	5.89	1698	C:O
6.06	6.06	1650	C:C
6.96	6.96	1437	Satd. CH_2
7.23	7.23	1383	C–CH_3
...	10.36	965	*trans* RCH=CHR′
14.29	...	700	*cis* RCH=CHR′

Rasmussen, Brattain and Zucco[9] have pointed out that the 10.3-micron band is characteristic of the *trans* form of the group RCH=CHR′, rather

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[1] Article not copyrighted.

[2] W. A. Gersdorff, *J. Econ. Entomol.*, (a) **40**, 878 (1947); (b) **42**, 532 (1949).

[3] Milton S. Schechter, Nathan Green and F. B. LaForge, THIS JOURNAL, **71**, 3165 (1949).

[4] Stanley H. Harper, *J. Chem. Soc.*, 892–895 (1946).

[5] Since the spectra presented in this paper were obtained, the synthesis of (±)-*cis*-cinerolone has been announced: L. Crombie and S. H. Harper, *Nature*, **164**, 534 (1949).

[6] The author expresses his appreciation to M. S. Schechter, N. Green and F. B. LaForge for the samples used in this work, and for their respective physical constants. Synthetic 2-(2-butenyl)-4-hydroxy-3-methyl-2-cyclopenten-1-one: b. p. 113–115° at 0.25 mm., $n^{25}\mathrm{D}$ 1.5132. Natural cinerolone, b. p. 118–120° at 0.2 mm., $n^{25}\mathrm{D}$ 1.5221. Although the natural cinerolone may not have been perfectly pure, the infrared spectrum shows no evidence of impurity. Both samples were regenerated from the semicarbazones.

[7] R. Bowling Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *ibid.*, **20**, 402–410 (1948).

[8] N. H. Cromwell, F. A. Miller, A. R. Johnson, R. J. Frank and D. J. Wallace, THIS JOURNAL, **71**, 3337–3342 (1949).

[9] R. S. Rasmussen, R. R. Brattain and P. S. Zucco, *J. Chem. Phys.*, **15**, 135–140 (1947).

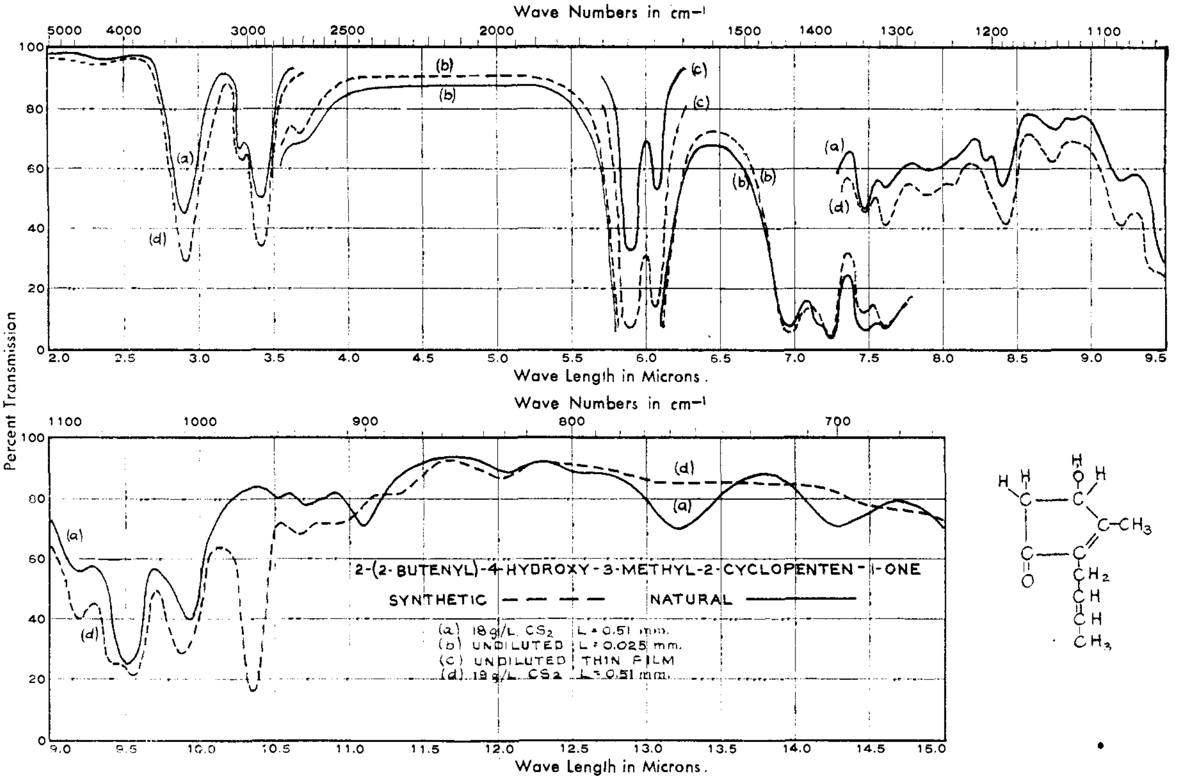

Fig. 1.

than of both *cis* and *trans* forms, as had been previously assumed. Kilpatrick and Pitzer,[10] in a vibrational analysis which included consideration of infrared and Raman data of other workers, assigned the 10.37-micron infrared band of *trans*-2 butene to a wagging vibration of the two hydrogen atoms out of the plane of the carbon skeleton. Anderson and Seyfried[11] empirically assigned normal band positions for various functional groups in oxygenated and olefin-type compounds as found in synthesis-type naphthas. They include a *trans* RCH=CHR′ band at 10.36 ± 0.02 microns and a *cis* band at 14.0–14.6 microns. Fred and Putscher,[12] from a study of the source of the 10.3-micron band, which occurs in Pennsylvania lubricating oils, conclude that olefins with internal, unsubstituted, *trans* double bonds are the only class of hydrocarbons with a characteristic 10.3-micron band, although they point out that other compounds, including the alkyl cyclohexanes, may absorb in this region. They also state that *trans* olefins are apparently more abundant in nature than *cis* olefins, in accordance with their greater stability.

It may therefore be concluded that the infrared spectra presented in this paper show with reasonable certainty that the two compounds are *cis–trans* isomers, and that natural cinerolone is the *cis* form and the synthetic 2-(2-butenyl)-4-hydroxy-3-methyl-2-cyclopenten-1-one the *trans* form. This confirms the conclusions of Harper[4] and of Schechter, Green and LaForge.[6] In this case, therefore, it is found that the naturally occurring material is the *cis* form, which appears to be the less stable form.

Summary

Infrared spectra of natural cinerolone and synthetic 2-(2-butenyl)-4-hydroxy-3-methyl-2-cyclopenten-1-one have been obtained over the wavelength range of 2 to 15 microns. The spectra indicate that the compounds are *cis–trans* isomers, and that the naturally occurring compound is the *cis* form and the synthetic compound the *trans* form. The spectra confirm the molecular structures as determined by Harper and by LaForge and co-workers.

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(10) John E. Kilpatrick and Kenneth S. Pitzer, *J. Research Nat. Bur. Standards*, **38**, 191–209 (1947).

(11) J. A. Anderson, Jr., and W. D. Seyfried, *Anal. Chem.*, **20**, 998–1006 (1948).

(12) Mark Fred and Richard Putscher, *Anal. Chem.*, **21**, 900–911 (1949).