

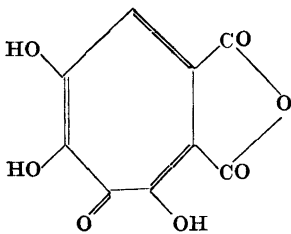
## Studies in the Tropolone Series

## III. Infra-red Spectra

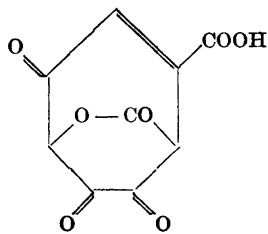
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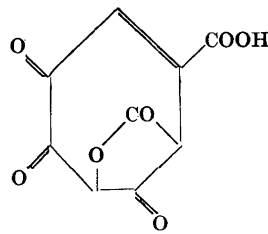
It was recently stated in a short note in this journal<sup>1</sup> that ultra-violet absorption studies on puberulonic acid<sup>2-4</sup> and related compounds at various hydrogen ion concentrations had led one of the present authors to propose a new formula (I) for the acid instead of the lactone structures (II) and (III) put



(I)



(II)



(III)

forward by Todd *et al.*<sup>4</sup>. In the same note it was briefly mentioned that the anhydride formula was also supported by infra-red absorption data. We understand that similar work in the infra-red field is now being done in other European and American laboratories and, hence, consider it justifiable to publish the results of our infra-red studies prior to those of the ultra-violet investigations although the chronological order is thereby reversed.

The main purpose of the present investigation was to confirm the structure (I) for puberulonic acid. This structure contains a tropolone skeleton and an acid anhydride ring, but no carboxyl group. The vibrational frequencies of these structural elements are known from earlier investigations on a variety of organic substances (*cf.* below). They are well-characterized although naturally somewhat influenced by neighbouring parts of the molecules. Hence, the

infra-red spectrum of a compound possessing structure (I) must be easily distinguishable from those of substances like (II) and (III), especially if compared with the spectra of closely related compounds. Stipitatic<sup>5-7</sup> and puberulic<sup>2-4</sup> acids as well as  $\beta$ - and  $\gamma$ -thujaplicins<sup>8,9</sup> were used as reference compounds in this investigation. In connection with this work, the infra-red spectrum of nootkatin<sup>10</sup> was also determined.

Some work on the infra-red absorption properties of tropolones has been reported during the current year. Scott and Tarbell<sup>11</sup> examined solutions of colchicine and some of its derivatives as well as  $\gamma$ -thujaplicin and  $\beta$ -methyltropolone. They found a series of three or four absorption bands in the region 1 255—1 625  $\text{cm}^{-1}$  which occurred in all the tropolone derivatives and were therefore considered typical for the tropolone ring system. The approximate wave-numbers of the bands were: 1 280, (1 350), 1 550 and 1 615  $\text{cm}^{-1}$ . In a later communication from the same laboratories<sup>12</sup> bands of similar wave-numbers were reported for 4,5-benzotropolone and derivatives thereof. A synthetic carbethoxytropolone was found by Bartels-Keith and Johnson<sup>13</sup> to exhibit absorption maxima at 1 250, 1 440, 1 478, 1 560 and 1 620  $\text{cm}^{-1}$  which were ascribed to the tropolone nucleus.

A comparison of the bands reported for tropolone derivatives shows that they all absorb in the following regions: 1 250—1 280, 1 538—1 567 and 1 605—1 624  $\text{cm}^{-1}$ . For  $\beta$ -methyltropolone and  $\gamma$ -thujaplicin, in the 1 450—1 500  $\text{cm}^{-1}$  region (*cf.* the 1 478 band of carbethoxytropolone), Scott and Tarbell observed general absorption but no well-defined bands. Not only structural differences between the substances but also the solvents employed cause minor variations in the wave-numbers of the maxima.

#### EXPERIMENTAL

The samples\* were investigated in the form of paraffin smears (1 part of the sample in approximately 8 parts of paraffin except for puberulonic acid, where the ratio was 1 : 2.5). Transmission of 0.025 mm layers was determined with a Perkin-Elmer Model 12 B infra-red spectrometer using a rock salt prism. The slit-width was varied with the wave-numbers according to the following scheme (wave-numbers in  $\text{cm}^{-1}$ , slit-widths in mm in parentheses): 662—738 (0.520), —904 (0.230), —1 052 (0.177), —1 309 (0.097), —1 552 (0.069), —1 987 (0.033), —2 000 (0.015).

\* The provision of pure specimens of puberulonic, stipitatic and puberulic acids by Professor H. Raistrick, and of the thujaplicins and nootkatin by Professor H. Erdtman is gratefully acknowledged.

## RESULTS AND DISCUSSION

Fig. 1 shows the percentage absorption curves and Table 1 gives the wave-numbers for the bands of main interest. It is seen that all of the substances investigated exhibit absorption bands within, or very close to, the three regions mentioned above as being characteristic for the tropolone nucleus. This, of course, furnishes strong evidence in favour of the tropolone structure for

Table 1.

Substance	Wave-numbers of bands ( $\text{cm}^{-1}$ )				
$\beta$ -Thujaplicin	1 270	(1 480)	1 545	1 615	
$\gamma$ -Thujaplicin	1 265	(1 490)	1 560	1 605, 1 620	
Stipitatic acid	1 285	(1 480)	1 570	1 615	1 700
Puberulic acid	1 285	1 505	1 535	1 595	1 680
Puberulonic acid	1 285	1 505	1 545	1 620	1 770 1 830
Nootkatin	1 270	(1 480)	1 550	1 595	

puberulonic acid and the tropolone structure of nootkatin is also confirmed.

The 1 480—1 505  $\text{cm}^{-1}$  maxima are most probably analogous to the 1 478  $\text{cm}^{-1}$  band for carbethoxytropolone and also ascribable to the tropolone ring system.

The strong absorption maxima at 1 680 and 1 700  $\text{cm}^{-1}$  for puberulic and stipitatic acids respectively are due to the carboxyl groups<sup>14</sup>. The absence of a corresponding maximum in the puberulonic acid absorption curve is inconsistent with the two formulae (II) and (III).

The intense bands at 1 770 and 1 830  $\text{cm}^{-1}$ , exhibited by puberulonic acid alone, constitute the pair typical for acid anhydrides. The exact position of this pair varies with the structure of the anhydride concerned. The wave-numbers found for puberulonic acid, however, agree well with *e. g.* the approximate values 1 775 and 1 845  $\text{cm}^{-1}$  for phthalic anhydride<sup>14</sup> and 1 795 and 1 850 for maleic anhydride<sup>14</sup>.

The results reported above, together with chemical and ultra-violet spectral evidence, conclusively establish that puberulonic acid is (I) or a tautomeride thereof, differing in the arrangement of the nuclear CO and —OH groups. This mould metabolite, puberulonic acid, discovered by Birkinshaw and Raistrick in 1932, is thus not only a tropolone but also one of the rare naturally-occurring acid anhydrides.

For nootkatin, the infra-red data together with ultra-violet evidence<sup>10</sup> shows that this substance also is a tropolone. Chemical investigation<sup>15</sup> (isolation of acetone as a degradation product) shows that it contains an isopropylidene group, but the infra-red absorption curve offers no certain evidence

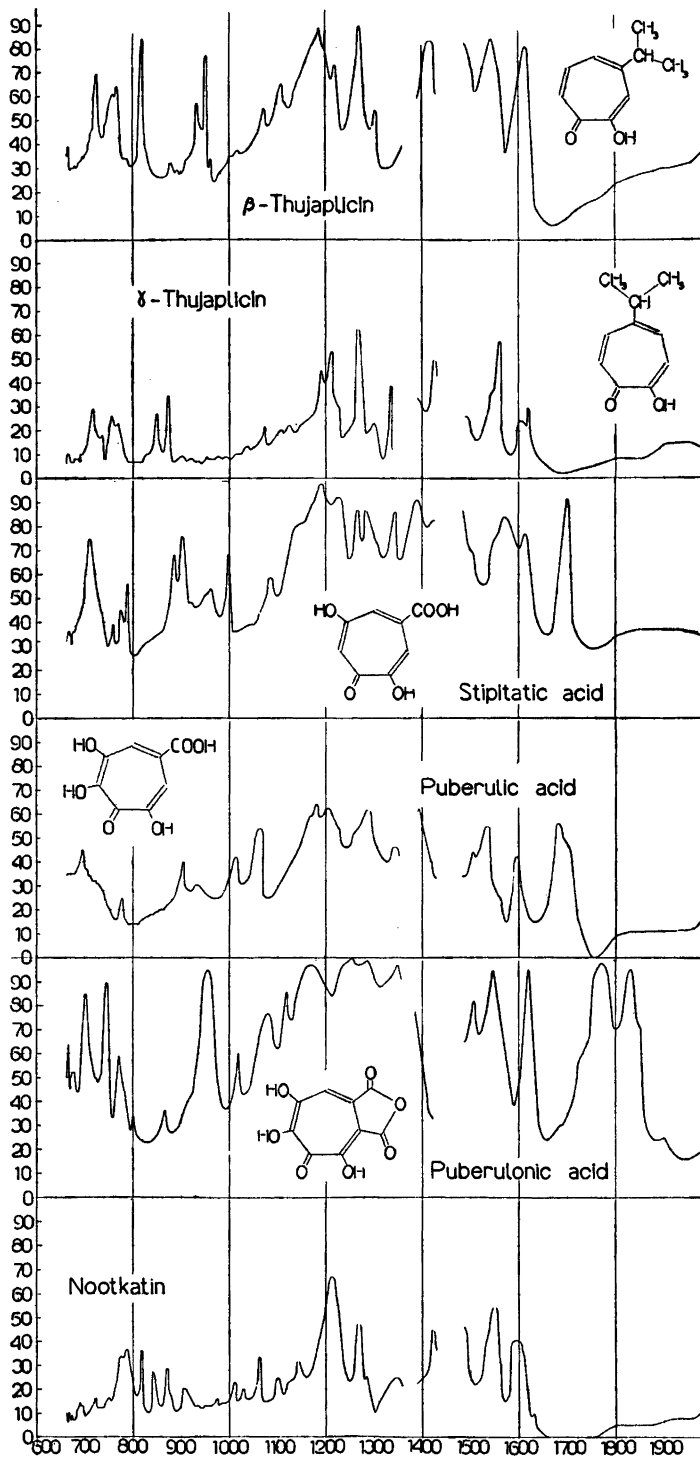


Fig. 1. Percentage absorption. Wave-numbers in cm<sup>-1</sup>.

regarding the existence of an extra-nuclear double bond in the molecule. Its stretching band may, however, be obscured by the tropolone band at  $1595\text{ cm}^{-1}$ .

#### SUMMARY

Infra-red spectra have been determined for paraffin smears of puberulonic, puberulic and stipitatic acids,  $\beta$ - and  $\gamma$ -thujaplicins and nootkatin. Four maxima, characteristic for the tropolone ring system, were found in all cases. No carboxyl band but anhydride bands at  $1770$  and  $1830\text{ cm}^{-1}$  were found in the puberulonic acid curve. This shows that puberulonic acid possesses structure (I) or a tautomeric formula, not the structure (II) or (III). The formula (I) has been suggested earlier on the basis of ultra-violet spectroscopic evidence.

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