

idea of coexistent crystalline and amorphous regions in polymers might be deficient and represent a too simple concept. HOSEMANN has developed a theory of the paracrystalline state which would give rise to similar patterns of X-ray scattering. This has led to some confusion and even put in doubt as to whether previous quantitative conclusions on the degree of crystallinity of polymers make any real sense.

Recent work by RULAND, introducing some new rigid principles, has shown that in polyolefins at least, the two-phase system of a well-ordered crystalline phase coexisting with an amorphous one, must very nearly approach reality. His procedure yields figures

for the degree of crystallinity which, in the case of polypropylene, appeared to be well in line with those obtained by the older, much more simple, relative method of evaluation worked out by the present author.

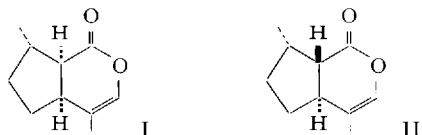
In the case of the nylons RULAND found somewhat more complicated conditions and had to conclude that, besides a still predominant, well-ordered, crystalline phase, a certain fraction of the polymer substance—which he tends to identify with the so-called hexagonal  $\beta$ -modification—rather represents a state of disorder corresponding to HOSEMANN's paracrystalline state. In this case application of the simple classical methods would give rise to incorrect results.

## Brèves communications – Kurze Mitteilungen – Brevi comunicazioni – Brief Reports

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### Terpenoids. *Cis-trans-* and *trans-cis-* Nepetalactones<sup>1</sup>

A mixture containing *cis-trans*-nepetalactone (I) and *trans-cis*-nepetalactone (II) has been shown to possess the cat-attracting activity of *Nepeta cataria*, commonly termed 'catnip'<sup>2</sup>. Early efforts to separate these stereoisomers failed<sup>2b</sup>. We wish to report a method for separating them, and to record some properties of the purified materials.



Of several vapor phase chromatographic columns tried, only a polar silicone column (1/4 inch in diameter, 5 feet long, containing 20% Dow Corning QF-1 on 60/80 firebrick, usually used at 209°) was effective for the separation of a mixture of nepetalactones obtained by vacuum distillation of oil of catnip from Fritzsche Brothers Inc. The separation was not complete, but the mixture could be estimated to contain 75 ± 5% of I (retention time, 15 1/2 min) and 25 ± 5% of II (17 min), and collection of the first half of the first peak gave I in which no II could be detected (VPC) and of the last half of the second peak, II containing 16% of I. A second passage of this 84% I through the column, again collecting the last half of the second peak, gave essentially pure II.

The structural assignments for the separated nepetalactones are clear from previous chemical studies, which showed the nepetalactone mixture to contain at least 51% of I and 26% of II<sup>2b</sup>. For confirmation, the purified I was treated with ozone followed by sodium borohydride, yielding nepetalactones<sup>2b</sup>. The spectra of the purified nepetalactones as described below are consistent with the proposed structures.

The infrared spectra of I and II are similar in the double bond region and in most of the fingerprint region, but I can readily be distinguished by its peak at 1200 cm<sup>-1</sup>, and II by peaks at 1065 and 905 cm<sup>-1</sup>. The nuclear magnetic resonance spectra (in DCCl<sub>3</sub>) are also similar, but showed slight differences in certain chemical shifts: in I, the methyl group attached to the double bond absorbs at 8.34  $\tau$ , the other methyl group at 8.78  $\tau$ , and the vinyl proton at 3.75  $\tau$ ; in II, the corresponding protons absorb at 8.27, 8.87, and 3.72 respectively. Both compounds had  $n_D^{25}$  1.4878 ± 0.0001. I had  $[\alpha]_D^{27.5} + 11.1^\circ$  (CHCl<sub>3</sub>) and the mixture containing 84% of II, +20.2°; the calculated rotation of pure II is thus +21.9°<sup>3</sup>.

Finally, bioassays were conducted with the purest materials obtained. Ethanol solutions of each of the isomers were applied to cotton balls, and most of the solvent was allowed to evaporate. The balls (and numerous blanks, prepared with ethanol) were made available to eight cats. Three were strongly attracted to the balls containing II, two showed slight preference for them, and two were indifferent to all of the balls. Thus, the minor isomer, II, is definitely active. Whether or not the major isomer possesses any activity could not be decided; one of the cats was definitely more interested in the ball containing I than in the blanks, but the small amount of II

<sup>1</sup> Terpenoids VIII.

<sup>2</sup> (a) S. M. McELVAIN, P. M. WALTERS, and R. D. BRIGHT, J. Amer. chem. Soc. 64, 1828 (1942). – (b) R. B. BATES, E. J. EISENBRAUN, and S. M. McELVAIN, J. Amer. chem. Soc. 80, 3420 (1958), and references cited therein.

<sup>3</sup> For nepetalactones distilled from oil of catnip,  $[\alpha]_D^{23} - 13.0^\circ$  (CHCl<sub>3</sub>) has been reported, and for nepetalactones from the pyrolysis of nepetalic acid, +3.6° (S. M. McELVAIN, R. D. BRIGHT, and P. R. JOHNSON, J. Amer. chem. Soc. 63, 1558 (1941)). These preparations probably contained small amounts of a strongly levorotatory impurity.

present as an impurity may have been responsible for this interest. Racemic I has been synthesized, but no mention was made of tests with cats<sup>4,5</sup>.

**Zusammenfassung.** Die beiden stereoisomeren Nepetalactone wurden durch Gaschromatographie getrennt. Es wurde gezeigt, dass das *trans-cis*-Isomere (II) auf Katzen anziehend wirkt. Das *cis-trans*-Isomere (I), das etwa 75% der Mischung darstellt, ist bedeutend weniger aktiv, möglicherweise völlig inaktiv.

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<sup>4</sup> T. SAKAN, A. FUJINO, F. MURAI, A. SUZUI, and Y. BUTSUGAN, Bull. Chem. Soc. Japan 33, 1737 (1960).

<sup>5</sup> The authors gratefully acknowledge financial support from the U.S. Public Health Service (GM-07689).

### Zur Konstitution von Helvolinsäure und Cephalosporin P<sub>1</sub>

DJERASSI et al.<sup>1</sup> haben kürzlich durch massenspektrometrische Untersuchung gezeigt, dass Helvolinsäure, ein Antibiotikum aus *Aspergillus fumigatus*<sup>2</sup>, die Zusammensetzung C<sub>33</sub>H<sub>44</sub>O<sub>8</sub> besitzt, wodurch die früher aufgestellte Formel I<sup>3</sup>, entspricht C<sub>32</sub>H<sub>42</sub>O<sub>8</sub>, revisionsbedürftig geworden ist. Auch die für Cephalosporin P<sub>1</sub>, eine antibiotische Substanz aus Cephalosporium-Stämmen, vorgeschlagene Formel II<sup>4</sup>, entspricht C<sub>32</sub>H<sub>42</sub>O<sub>8</sub>, ist nicht kongruent mit der neuerdings zu C<sub>33</sub>H<sub>50</sub>O<sub>8</sub> ermittelten<sup>5</sup> Zusammensetzung dieser Verbindung. Bereits von anderer Seite<sup>6</sup> ist auf eine mögliche Verwandtschaft dieser zwei Antibiotika mit der Fusidinsäure, einem biologisch wirksamen Metaboliten aus Fusidium-Stämmen, hingewiesen worden. Für diese letztere ist inzwischen auf Grund neuerer Experimente die Konstitutionsformel III (R = H) gesichert worden<sup>7</sup>, welche sich lediglich in der Haftstelle einer Hydroxylgruppe von einem früheren Vorschlag<sup>6</sup> unterscheidet.

Wir haben die NMR-Spektren der kristallinen Methylester der drei Antibiotika aufgenommen<sup>8</sup>. Die dabei erhaltenen, in der Tabelle zusammengestellten Daten sprechen ebenfalls gegen die früher angenommenen Formeln I und II von Helvolinsäure und Cephalosporin P<sub>1</sub> und beweisen, dass das bisher vermisste Kohlenstoffatom in beiden Fällen als tertiär gebundene Methylgruppe vorhanden ist.

Das NMR-Spektrum des Helvolinsäure-methylesters (vgl. Figur) zeigt, dass beide Acetoxygruppen an Kohlenstoffatomen haften, welche je ein Wasserstoffatom tragen. Die Lage und Multiplizität des Signals eines der beiden Protonen stimmt genau überein mit derjenigen des C<sub>16</sub>-Protons von Fusidinsäure-methylester, III (R = CH<sub>3</sub>). Da das gleiche Signal auch im NMR-Spektrum des Methylesters von Cephalosporin P<sub>1</sub> vorhanden ist, zwingt sich die

Vermutung auf, dass beide Verbindungen im fünfgliedrigen Ring ähnliche Substitutionsverhältnisse wie die Fusidinsäure aufweisen, und dass die Verwandtschaft zu dieser letzteren eine engere ist als bisher vermutet. Die bekannte

