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On Polyenic and Polyynic Compounds in *Centaurea cyanus* L.

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It has already been shown [1] that at least two compounds, "Centaur X" and "Centaur Y", with highly characteristic absorption spectra in the ultraviolet, occur in Centaurea species (*C. cyanus* L., *C. jacea* L., and *C. scabiosa* L.). The compounds were found in the lipophilic solvent extracts of the herbs. Later, Stavholt and Sørensen [2] found a compound in *Artemisia vulgaris* L. with a spectrum almost identical with that of our CX-comp.*, *i.e.* they have the same chromophoric system. Even at an early stage in our investigations, we could not exclude the possibility of CX and CY spectra belonging to more than two compounds (*cf.* the earlier paper). We made many attempts to get a further fractionating. As the usual routine methods failed, we applied the countercurrent distribution principle.

A preparation, obtained by distillation in vacuo (115—165° / $5 \cdot 10^{-3}$ mm) of a chlorophyll free ethereal fraction (*cf.* the earlier paper), was distributed between cyclohexane and 90 % methanol, the cyclohexane being the mobile phase. The number of transfers was 49. The spectroscopic analysis showed the presence of a highly complicated component system. At least four CX and two CY components could be demonstrated.

The CX components formed two groups with strongly different partition coefficients ($K_{C_6H_{12}/MeOH}$), on the one hand CX_1 and CX_2 with $K = 0.14$ and 0.19 respectively; on the other CX_3 and CX_4 with $K = 5.1$ and 7.2 respectively. The two CY components have K values = 0.75 and 11. The CX compounds have, surprisingly enough, only two spectra, one belonging to CX_1 and CX_3 and the other to CX_2 and CX_4. The two CY compounds have identical spectra.

* C denotes Centaur.

From a preparative point of view, the experiment indicates that the countercurrent distribution method may be useful for an isolation of CY_1 and possibly of CY_2. but that the other compounds can be separated only with great difficulty.

It seems obvious to us that CX_1 and CX_3 belong to one group with the same chromophoric system, whereas CX_2 and CX_4 belong to another such group; CY_1 and CY_2 are also chromophorically identical compounds.

Table 1 shows λ_{max} of the absorption spectrum of Sørensen's CX compound compared with λ_{max} of our CX_1 or CX_3 compound.

Table 1. Comparison between the absorption bands of Centaur X_1 or X_3 (measurements in cyclohexane) and of Sørensen's Centaur X compound (measurements in hexane); λ_{max} in Å and ν_{max} in sec^{-1}.

λ_{max} of Sørensen's Centaur X (hexane)	3485,	3260,	3064,	2895,	2694,	2592,	—
λ_{max} of Centaur X_1 or X_3 (cyclohexane)	3500,	3270,	3070,	2905,	2705,	2600,	2555
$\nu_{max} \cdot 10^{-12}$	857,	917,	977,	1033,	1109,	1154,	1174
$\Delta\nu$		60	60	56			

As will be seen from Table 1 the compounds have almost the same spectrum. The main difference is that there is a very weak band at 2555 Å, which is absent in Sørensen's CX compound. The positions of the absorption maxima of the CX_2 or CX_4 compounds are shown in Table 2.

Table 2. Absorption bands of Centaur X_2 or X_4 (measurements in cyclohexane); λ_{max} in Å and ν_{max} in sec^{-1}.

λ_{max} of Centaur X_2 or X_4 (cyclohexane)	3395,	3170,	2985,	2450
$\nu_{max} \cdot 10^{-12}$	884,	946,	1005,	1224
$\Delta\nu$		62	59	

It may be mentioned that the absorption curve of Sørensen's CX compound shows small inflexions or perturbations at the same places as our CX_2 or CX_4 have their maxima. The value $\triangle \nu \sim 60 \cdot 10^{12}$ sec^{-1} occurring in all CX compounds indicates the presence of carbon-carbon tripple bonds. In a recent investigation Cook, Jones and Whiting [3] synthesized acetylenic compounds of the type

$$CH_3 - CH = CH - (C \equiv C)_n - CH = CH - CH_3$$

and measured their spectra. When $n = 3$ surprising agreement with Sørensen's and our values is obtained as is seen from Table 3, which gives the positions of λ_{max} for the synthetic compound.

Table 3. Absorption bands of compound $CH_3 - CH = CH - (C \equiv C)_3 - CH = CH - CH_3$ *according to C. Cook, E. Jones and M. Whiting (measurements in ethanol);* λ_{max} *in Å.*

λ_{max}	3485,	3250,	3055,	2890,	2690,	2590,	2450–2500 *,	1990

As is seen from Table 3, Cook *et al.* found a band at 1990 Å, which was not given by Sørensen or by us. In our case, we have not made measurements in this short-wave region.

It seems obvious that both CX_1 or CX_3 and Sørensen's CX compound have the sama chromophoric system as the synthetic compound

$$CH_3 - CH = CH - C \equiv C - C \equiv C - C \equiv C - CH = CH - CH_3$$

The two Y compounds CY_1 and CY_2 have identical spectra of quite another type, *cf.* Table 4 and Fig. 1.

Table 4. The absorption bands of Centaur Y_1 *or* Y_2 *(measurements in cyclohexane);* λ_{max} *in Å and* ν_{max} *in* sec^{-1}.

λ_{max} of Centaur Y_1 or Y_2 (cyclohexane)	3195,	3045,	2915,	2800 **
$\nu_{max} \cdot 10^{-12}$	939,	985,	1029,	1071
$\Delta\nu$		46	44	42

Hexatriene-1,3,5 [4], octatetraene-1,3,5,7 [5] and phytofluene [6], which are all polyenes with three, four, and five conjugated double bonds, respectively, have similar spectra. According to Hausser, Kuhn and Seitz [7] conjugated polyenes at −196° have two different values of $\Delta\nu$, $37.0 \cdot 10^{12}$ sec^{-1} and $47.1 \cdot 10^{12}$ sec^{-1}. At room temperature, however, the spectrum is more diffuse; $\Delta\nu$ then shows *one* intermediate value, often at about $44 \cdot 10^{12}$ sec^{-1}. It therefore seems evident to us that CY_1 or CY_2 contains conjugated double bonds.

For polyenes of the type

$$R - (CH = CH)_n - R$$

a simple quantitative relation *** exists between n and the position of the first band (that of the longest wave-length), λ_0:

$$\lambda_0 = k_1 \sqrt{n} + k_2 \qquad (1)$$

k_1 and k_2 are constants differing for the different types of homologous series.

* Inflexion.

** Inflexion point.

*** *Cf.* for instance, Eistert [8].

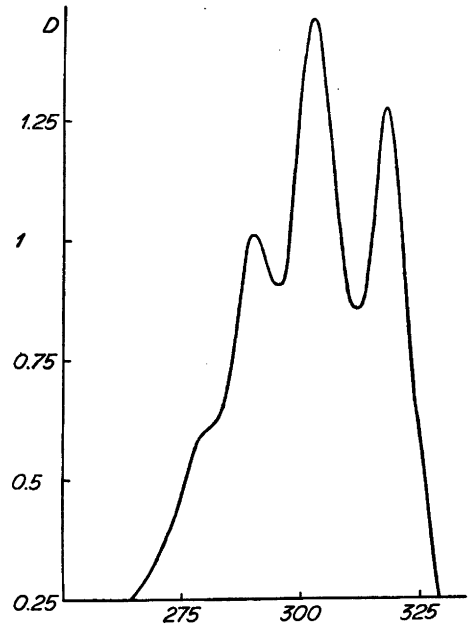

Fig. 1. The absorption spectrum of CY_1 *or* CY_2 *(measurements in cyclohexane); D = optical density.*

The first band of hexatriene [4] and octatetraene [5] are given in the literature at 2675 and 3040 Å respectively (measurements in cyclohexane). When inserting these values in (1) we will find $k_1 = 1362$ and $k_2 = 316$. From these values we are able to calculate λ_0 for decapentaene-1,3,5,7,9, equation (1) giving us $\lambda_0 = 3362$ Å. The first band of CY_1 or CY_2 has $\lambda_0 = 3195$ Å. We therefore assume that the compounds have a chromophoric system consisting of octatetraene with some bathochromic groups.

Values for some bathochromic groups, expressed as fractions of a new additional double bond (|=), are given by Kuhn and Grundmann [9]. For instance, a methyl group situated in the conjugated chain should be regarded as 1/4 |=.

In our case we may find the value of *one* new additional double bond by substracting the ν_0 value of decapentaene from that of octatetraene, giving us $\Delta\nu = 94.5 \cdot 10^{12}$ sec^{-1}. We may use this |= value in our calculations, not only for the first band but also for the others (*cf.* above). If the ν_{max} values of octatetraene are diminished by half the calculated |= value, the values obtained are in excellent agreement with the ν_{max} values of CY_1 or CY_2 found experimentally (*cf.* Table 5).

Table 5. The absorption bands of octatetraene (measurements in cyclohexane). Calculated band positions of dimethyloctatetraene compared with those of Centaur Y_1 or Y_2; λ_{max} in Å and ν_{max} in sec^{-1}.

λ_{max} of octatetraene (cyclohexane)	3040,	2905,	2780,	2678
$\nu_{max} \cdot 10^{-12}$	987,	1033,	1079,	1120
Decr. corresp. to two CH_3 groups $= 2 \cdot \frac{1}{4}\sqrt{\ }$	−47,	−47,	−47,	−47
Calc. $\nu_{max} \cdot 10^{-12}$ of $(Me)_2$-octatetraene	940,	986,	1032,	1073
Calc. λ_{max} of »	3191,	3042,	2907,	2796
Obs. λ_{max} of CY_1 or CY_2	3195,	3045,	2915,	2800

Hence our calculations indicate that CY_1 or CY_2 are octatetraene with 2 substituents, each equal spectroscopically to the methyl group. Though this result seems very plausible other possibilities cannot of course be excluded.

Decatetraene-2,4,6,8 (1,8-dimethyl-octatetraene-1,3,5,7) has been synthesized by Kuhn and Grundmann [10]. The first band of the CY compounds and of decatetraene have the same value, the other bands lie in the neighbourhood of each other though they do not agree very well (*cf.* Table 6).

Table 6. The absorption bands of Kuhn's decatetraene-2,4,6,8 (measurements in hexane); λ_{max} in Å and ν_{max} in sec^{-1}.

λ_{max} of Kuhn's decatetraene (hexane)	3200,	2970,	2830,	2720
$\nu_{max} \cdot 10^{-12}$	938,	1010,	1060,	1103
$\Delta\nu$		72	50	43

However, one of the $\Delta\nu$ values of the synthetic decatetraene seems to us rather peculiar ($72 \cdot 10^{12}$ sec^{-1}), and not characteristic of such a polyene. It is of interest to note that tetradecahexaene-2,4,6,8,10,12, synthesized by the same authors [10] does not show such a confusing $\Delta\nu$ value. (*Cf.* also for instance hexatriene, octatetraene and phytofluene, which show very constant and representative $\Delta\nu$ values.) The elementary analysis of the decatetraene is not quite acceptable, and the authors describe the compound as extraordinarily unstable, a fact that may perhaps have influenced the measurements.

It will be extremely difficult to isolate and characterize fully the CX and CY compounds present in the Centaurea species. CY_1 seems to us to be the only one of the compounds that can be isolated without too great difficulty. For this purpose a large amount of starting material will probably be necessary.

SUMMARY

It has been shown that *Centaurea cyanus* L. contains at least two compounds (Centaur X_1 and X_3) related to decadiene-1,9-triyne-3,5,7, and at least two compounds (Centaur Y_1 and Y_2) related to octatetraene-1,3,5,7.

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