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# Centaur X and Centaur Y. Two Unknown Substances in *Centaurea*-Species

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Spectrographic analysis in the ultraviolet has been carried out on alcohol extracts of the stalks and leaves of a large number of herbs, each of a different family.

Material from the cornflower, *Centaurea cyanus* L., showed a remarkable spectrum with a large number of bands. The same spectrum is also identifiable in *Centaurea jacea* L. and *Centaurea scabiosa* L., *i. e.* the two other *Centaurea*-species common in Sweden. The fraction which gives this spectrum is insolube in water but soluble in ether and has not previously been found in *Centaurea*-species. It is as yet impossible to state whether this fraction is to be found only in *Centaurea*-species. There is, nevertheless, no doubt that its occurrence in the flora is very rare.

It was found that the fraction in question was not uniform. By adsorption experiments on aluminium oxide and activated carbon it could be shown that the spectrum observed consisted of two spectra. The experiments were carried out as follows.

The fresh, finely ground stalks and leaves of *Centaurea cyanus* L. were extracted with ethanol until they were completely free from chlorophyll. After the addition of a large quantity of water the solution was extracted several times with ether. The strongly green-coloured ether solution was washed several times with water and then dried with sodium sulphate *. In this case an ethereal solution was prepared corresponding to 3.2 kg of fresh stalks and leaves per litre.

* A solution prepared in this way and stored for four years showed no change in the characteristic spectrum.

2.5 ml of 5 per cent methanolic potassium hydroxide solution was added to 20 ml of the ethereal solution. The mixture was shaken mechanically for two hours. A large quantity of water was added and the ether layer retained. This was then washed several times with water to remove the saponified chlorophyll; the washing must be done carefully in order to prevent emulsification. The resulting, strongly *yellow* ethereal solution was dried over-night with magnesium sulphate. The ether was evaporated and the residue dissolved in 20 ml of spectroscopically pure hexane. This solution again showed the characteristic spectrum of the original alcohol or ether solution (v. Fig. 1 a**).

As expected, the hexane solution gave a more distinct spectrophotogram than the other two solutions. The position of the absorption maxima of the bands is shown in Table 1, first row.

*Table 1. Absorption bands in the ultraviolet of the lipoid-soluble fraction in Centaurea cyanus. Components Centaur X and Centaur Y after chromatographic analysis. The errors in the wave-lengths are about 0.5 mμ.*

| Hexane solution of | Wave-lengths of absorption maxima mμ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Total fraction ..... | 350 | 320 | 305 | 290 | 278 | 269 | 259 | 254 | 244 |
| Centaur X ..... | 350 | 326 | 307 | | | 269 | 259 | 254 | 245 |
| Centaur Y ..... | | 319 | 305 | 291 | 278 | | | | |

The hexane solution was chromatographed on an aluminium oxide column (washing solution : pure hexane). The absorption in the ultraviolet of the outflowing solution was controlled by means of the quartz-spectrograph. The carotenoid pigments formed two zones: an upper, yellow, almost immobile zone and a moving reddish-yellow zone. It could be established with the quartz-spectrograph that the ultraviolet spectrum of the *colourless* solution that first issued from the column differed considerably from that of the original hexane solution***.

The two broad bands with maxima at 290 and 278 mμ (the latter band is extremely weak) could not be observed and the broad bands at 320 and 305 mμ were replaced by narrow bands at 326 and 307 mμ. The band at the

** For the photographs a high-voltage hydrogen lamp was used as a source of continuous radiation.

*** The strongly yellow-coloured pigments have nothing to do with the absorption bands described here. As shown later on, the initial spectrum can be separated into two spectra, both belonging to *colourless* fractions. Nor do the common carotenoid pigments absorb at these wave-lengths.

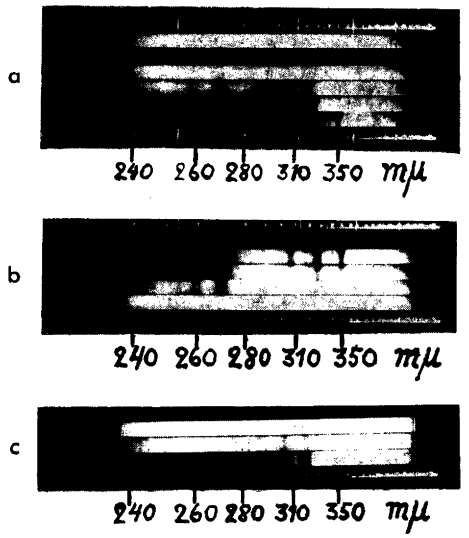


*Fig. 1. Absorption spectrum in hexane solution of*
*a) the lipoid-soluble fraction of Centaurea cyanus,*
*b) Centaur X,*
*c) Centaur Y.*

longer wave-lenght 350 mμ and the four bands at 269, 259, 254 and 244—245 mμ remained unaltered.

Hence it is obvious that the bands of the original solution cannot be caused by one uniform compound. At least two compounds must have formed the total spectrum of the original solution. Repeated passage of the fraction obtained through an aluminium oxide column did not change the spectral composition. It seems therefore very probable that this spectrum belongs to a uniform compound, which we provisionally call Centaur X. Fig. 1 b gives the spectrum of Centaur X, and the table gives the position of the bands measured.

From the lower half of the chromatogram described, the fraction which corresponds to the remaining part of the original spectrum can be eluated with methanol together with the »moving» lower carotenoid pigment. A spectrophotogram of this fraction dissolved in hexane (the methanol evaporated *in vacuo*) is shown in Fig. 1 c. The compound to which this spectrum belongs is provisionally called Centaur Y. The positions of the absorption maxima of the bands are shown in the table.

If the original hexane solution is treated with activated carbon instead of aluminium oxide, Centaur X is more strongly adsorbed than Centaur Y.

Hence, after shaking the solution with a suitable quantity of activated carbon, the spectrophotogram shows the characteristic picture of Centaur Y. The solution is colourless. Consequently, in addition to Centaur X, the yellow carotenoid pigments are also adsorbed by the carbon (*cf.* footnote ***).

It is worthy of note that the original hexane solution has bands at 320 m$\mu$ and 305 m$\mu$, of which the first is a combination of band 326 from Centaur X and band 319 from Centaur Y, and the latter is a combination of band 307 from Centaur X and band 305 from Centaur Y (*cf.* the table).

When shaking an ethereal solution containing Centaur X and Centaur Y with an acid or alkaline aqueous solution, the light absorption is not noticeably altered. It is therefore highly probable that the compounds are neutrals.

## SUMMARY

1. A fraction insoluble in water but soluble in ether and hexane and characterized by numerous bands in the ultraviolet region is demonstrated in three *Centaurea*-species commonly found in Sweden.

2. By means of chromatographic analysis it is possible to divide the fraction into two substances, each with characteristic spectra. The two substances are provisionally called Centaur X and Centaur Y.

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