

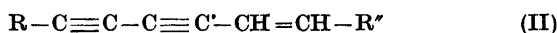
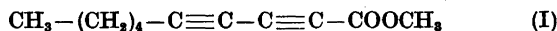
## Studies Related to Naturally Occurring Acetylene Compounds. XX. A Preliminary Communication on Some Polyacetylenic Pigments from *Compositae* Plants

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A reinvestigation of the essential oil from some species *Helipterum* rendered a complicated mixture of polyacetylenic compounds. Three of these, with first maximum at 3 985, 4 005 and 4 100 ÅU, respectively, were obtained spectroscopically pure. Of these, the first polyacetylenic pigments found in Nature, only the 4 100-pigment could be isolated in substance. The spectral properties of the 4 100-pigment point definitely to an ene-pentayne structure (V), the extreme instability corresponds well to that described for synthetic relatives. The very characteristic spectrum of (V) has so far been found in a dozen *Compositae* plants belonging to the tribes *Inuleae* og *Heliantheae*. Acetylenic pigments thus seem to be rather common in nature. The small concentrations in which they have been found and their instability may explain why they have not been detected before.

In the XIIth communication of this series<sup>1</sup> Skattebøl and Sørensen synthesised methyl deca-2 : 4-diyne-1 (I) with the object of obtaining the



U.V.-spectrum for comparison with an unknown chromophore with first U.V.-maxima at 2 862 and 2 650 ÅU found in essential oils from some species belonging to the genus *Helipterum*. The observed maxima of this *Helipterum* chromophore occurred at somewhat shorter wave-lengths than those of enediynes (II). (I) turned out to have maxima at somewhat longer wave-lengths than (II), and so we had to return to an investigation of new samples of essential oils from *Helipterum*. In the meantime the problem had considerably altered since it on a spectroscopical investigation of a small sample of the essential oil from *Gnaphalium luteo-album* L. root was observed that this oil had

strong maxima in the same positions 2 865 and 2 650 ÅU as the *Helipterum* oils, but besides these strong maxima the *Gnaphalium* oil had very weak but extremely sharp maxima at 4 100, 3 780, 3 290 and 3 075 ÅU, and when this oil was investigated chromatographically it turned out that the weak long-waved band group belonged to the same substance as the 2 865 and 2 650 ÅU maxima. The same turned out to be the case also for *Helipterum* oils when new samples became available.

The *Gnaphalium luteo-album* had been drawn from a seed sample most kindly put at our disposal by Dr. K. Bisvas, superintendent of the Indian Botanic Garden, Calcutta, who on the request of professor Dr. Ove Arbo-Høeg had sent us a small collection of seeds of Indian *Compositae*. This collection consisted partly of seeds from some widely distributed tropical weeds. The selection of these samples was for our purposes the most lucky one, as all of them turned out to be rich in polyacetylenic compounds and some of them contained the chromophore with first maximum at 4 100 ÅU. As described in the experimental part this chromophore — the first polyacetylenic pigment observed in Nature — has so far been spectroscopically indicated in the root of the following plants:

|  | Tribe and subtribe according to Hofmann <sup>2</sup> |                      |
|--|--|----------------------|
| <i>Blumea lacera</i> D. C.               | <i>Inuleae</i>                                       | <i>Plucheinae</i>    |
| <i>Blumea lacinata</i> D. C.             | »  | »                    |
| <i>Gnaphalium luteo-album</i> L.         | »  | <i>Gnaphalinae</i>   |
| <i>Gnaphalium silvaticum</i> L.          | »  | »                    |
| <i>Helipterum Manglesii</i> F. V. Muell. | »  | »                    |
| <i>Helipterum roseum</i> Benth.          | »  | »                    |
| <i>Helipterum Sandfordii</i>             | »  | »                    |
| <i>Pulicaria vulgaris</i> Gaertn.        | »  | <i>Inulinae</i>      |
| <i>Xanthium strumarium</i> L.            | <i>Heliantheae</i>                                   | <i>Ambrosinae</i>    |
| <i>Xanthium</i> , unknown sp.            | »  | »                    |
| <i>Sanvitalia procumbens</i> Lam.        | »  | <i>Zinninae</i>      |
| <i>Synedrella nudiflora</i> Gaertn.      | »  | <i>Coreopsidinae</i> |

Thus this pigment seems to have a rather wide occurrence. The amounts present in essential oils or acetone extracts are mostly so small that only a few of the strongest U.V.-absorption maxima stand out on the general step out towards shorter wave-lengths generally met in crude oils.

Acetone extracts of the root of *Helipterum Manglesii* F. v. Muell. and *Helipterum roseum* Benth. have given the highest amounts of the 4 100-pigment and have permitted a preliminary study of the structure. These extracts contained a complex mixture of substances with selective absorption in U.V. So far we think that only 3 of them have been obtained spectroscopically pure; only the 4 100-pigment was present in sufficient amount to be isolated in substance.

When these *Helipterum Manglesii* & *H. roseum* root extracts were chromatographed on slightly deactivated alumina<sup>3</sup>, 1—2 % benzene in petroleum ether eluted a slightly yellow substance with the U.V.-spectrum reproduced in Fig. 1 curve B, first maximum 4 005 ÅU. With the first washings with 5 % benzene in the petroleum ether there followed mixtures of this 4 005 chromo-

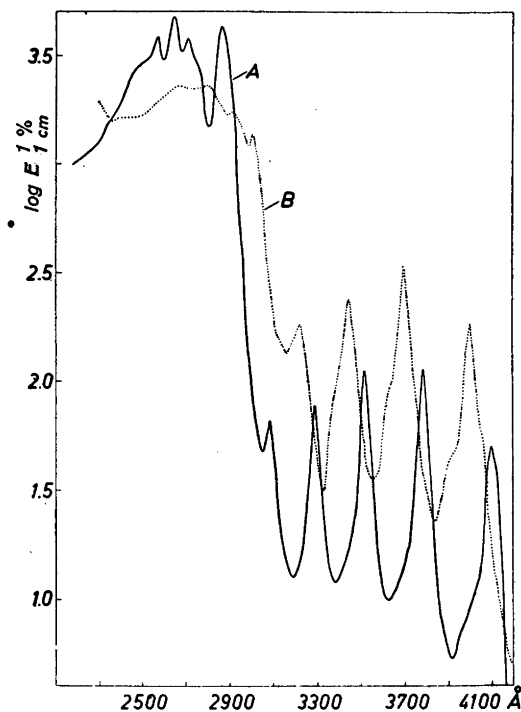
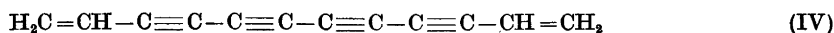


Fig. 1. Ultraviolet absorption in hexane of  
 A: 4 100-pigment from *Helipterum*, B: 4 005-pigment from *Helipterum*.

phore with the 4 100-pigment. With the later washings with 5 % benzene in petroleum the 4 100-pigment may sometimes be obtained quite pure. When evaporated *in vacuo* at room temperature this solution gives a residue of yellow elongated prisms, which turn black and insoluble at room temperature in some minutes. When stored at  $-15^{\circ}$  they acquire a bronze-coloured surface in a few minutes and when redissolved a dark pattern of the surface of the crystals are left as an insoluble residue on the wall.

The U.V.-spectrum of the crystalline 4 100-pigment is given in Fig. 1, curve A. As the extreme instability described above prevents all exact operations on a balance the extinction coefficient is rather uncertain.

The U.V.-spectrum of the 4 100-pigment has the same general shape as those of the symmetrical diene-polyenes synthesised by E. R. H. Jones *et al.*<sup>4</sup>, *cf.* our XVIIth communication<sup>5</sup> where the spectrum of tetradeca-2 : 12-diene-4 : 6 : 8 : 10-tetrayne (III) is reproduced together with the spectrum of dodeca-



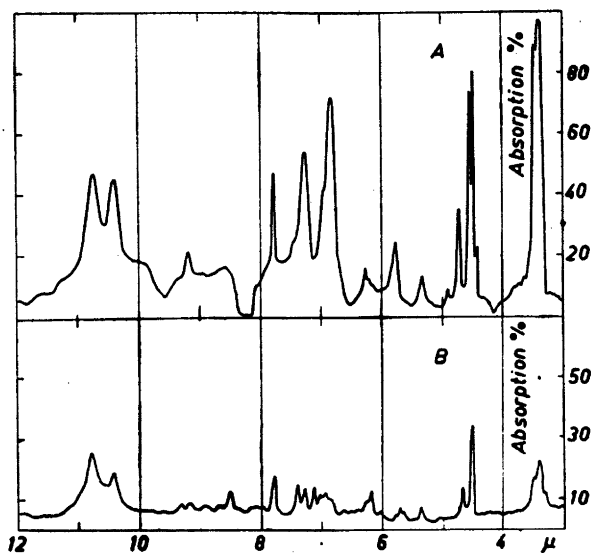


Fig. 2. Infrared absorption of

- A: 4 100-pigment in  $\text{CHCl}_3$ ,  $c = \text{ca. } 18\%$ ,  $l = 0.05 \text{ mm}$ , solution contaminated with spectral hexane.  
 B: dodeca-1:11-diene-3:5:7:9-tetrayne in  $\text{CCl}_4$ ,  $c = 7\%$ ,  $l = 0.05 \text{ mm}$ .

1:11-diene-3:5:7:9-tetrayne (IV) isolated from some *Compositae* plants\*. It is remarkable that 3 of the maxima in the strong short-waved group, viz. 2 863, 2 705 and 2 570 ÅU occur in nearly identical positions in the spectrum of the 4 100-pigment and in the spectra of (III) and (IV). The long-waved band group of the *Helipterum*-pigment, however, is displaced some 120 ÅU towards longer wave-lengths relative to (III), some 185 ÅU relative to (IV). Besides this displacement of the long-waved band group at longer wave-lengths the most interesting feature is that the difference in intensity of the two band groups is about 1.0 in  $\log \epsilon$  in the spectra of (III) and (IV) whereas it amounts to no less than 1.5 in  $\log \epsilon$  in that of the 4 100-pigment.

From the numerous spectra of synthetic polyene-yne<sup>4,6,7</sup> and poly-yne<sup>8</sup> we know that the difference between the intensity of the two band groups are the greater the more we approach the pure poly-yne, where the difference in dialkylpoly-yne is  $\sim 3.0$ .

That the 4 100-pigment still contains at least one double bond is shown by the infra-red spectrum reproduced in Fig. 2, curve A, together with that of IV, curve B; both have the vinyl band in the position of vinylacetylenes, at 933, 962 and 1 870  $\text{cm}^{-1}$ . The intensity and complexity of the acetylenic band group about 2 200  $\text{cm}^{-1}$  is the strongest so far met with in the infra-red spectra of naturally occurring acetylenes.

\* Cf. foot-note page 1743.

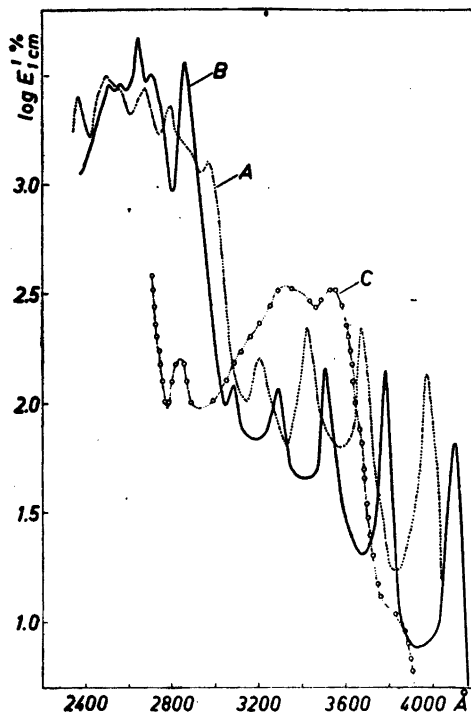


Fig. 3. Ultraviolet absorption in hexane of

A: 3 985-pigment from *Helipterum*. B: 4 100-pigment from *Xanthium*.  
C: polyene fraction from *Helipterum*.

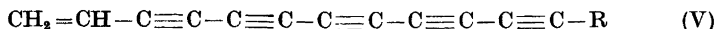
So far no vinyl-penta-acetylene is known. The U.V.-spectrum of that type must be intermediate between that of dialkyl-hexaynes and the divinyl-tetrayne (IV):

|          |   |       |       |       |             |    |
|----------|---|-------|-------|-------|-------------|----|
|          | $R-C\equiv C-(C\equiv C)_4-C\equiv C-R^{6,7}$ | 4 300 | 3 925 | 3 605 | 3 385       | AU |
|          | $CH_2=CH-(C\equiv C)_4-CH=CH_2^5$             | 3 905 | 3 610 | 3 370 | 3 160       | ,  |
| Mean     | $R-C\equiv C-(C\equiv C)_4-CH=CH_2$           | 4 100 | 3 768 | 3 488 | 3 273       | ,  |
| Observed | <i>Helipterum</i> chromophore:                | 4 100 | 3 780 | 3 515 | 3 285 3 080 | ,  |

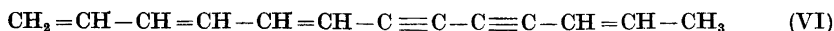
The agreement is, as will be seen, very satisfactory as the data is taken from measurements in different solvents.

Thus the 4 100-chromophore should be an enepentayne. As to the nature of the residue R the amounts available have not permitted quite conclusive experiments. The catalytical hydrogenation of a small amount of the crystalline compound furnished a perhydro compound of m.p.  $-14^\circ$ , in amounts insufficient for recrystallisation.  $R = H$ , which should be excluded because of the instability of monoalkyl-poly-yne, corresponds to the perhydro compound dodecane

m.p.  $-9,6^{\circ}$ . R = CH<sub>3</sub> corresponds to tridecane m.p.  $-5,3^{\circ}$ . The constitutional formula of the 4 100-chromophore thus might be given as (V)



where R may be CH<sub>3</sub>, (V) is the hexa-dehydro-derivative of the tetraenediynes (VI) isolated recently from some *Coreopsis* species:



When the percentage of benzene in the petroleum ether was raised to about 20, a complex mixture of compounds was eluted. One of the components has a rather broad maximum in U.V. at 4 300 ÅU, we have so far not been able to obtain the substance responsible for this maximum in a pure state. We have, however, succeeded in obtaining one component of this mixture, with regard to the U.V.-spectrum very similar to the 4 005-chromophore in a spectroscopically pure state, cf. Fig. 3, curve A. The difference in the position of the maxima of the two compounds are only some 20 ÅU. The amounts of the two chromophores with first max. at a little above and below 4 000 ÅU was too small to permit further investigations.

#### EXPERIMENTAL

*Helipterum*. The different garden varieties of *Helipterum*, viz., *H. Manglesii* (Nos. 4012, 4014 and 4016) *H. roseum* (No. 4020) *H. Sandfordii* (No. 4025) (seeds from A/S Norsk Frø) were cultivated at Norges Tekniske Høgskole during the summers 1952 and 1953.

|                  | Essential oil<br>Mean value<br>‰ | U.V.-absorption                                   |
|------------------|----------------------------------|---|
| Flowers          | 0.05                             | no selective abs., step out below 3 500 ÅU        |
| Leaves and stems | 0.05                             | no selective abs., almost step out below 3 500 ÅU |

The roots were repeatedly extracted with acetone at room temperature, the lipids transferred to petroleum ether and this solution chromatographed on alumina. The petroleum ether washings contained only substances with selective absorption below 2 600 ÅU. The washings with 1 % benzene eluted the 4 005-chromophore; increasing the amount of benzene to 5 % brought out mixtures of the 4 005 and the 4 100-chromophore. The tail of the 5 % benzene washings contained the pure 4 100-pigment. Since the subsequent 20 % benzene eluates turned out to be very complex mixtures, the column was emptied with ethyl ether, the solvents removed in a vacuum and the chromatography started the next day from 20 % benzene onwards. After small amounts of the 4 100-chromophore there followed a complex orange-red mixture of substances. The orange colour belonged to a substance with first maximum at 4 380 ÅU which, however, could never be obtained pure. A polyenic chromophore with rather broad and undistinct maxima at 3 545 and 3 320 ÅU, cf. Fig. 3, curve C, was eluted somewhat easier than the 4 300-pigment; in the later fractions the 3 985-chromophore dominated. This last substance, with the striking spectral conformity with the 4 005-pigment, could be separated completely by rechromatography from the 4 300-pigment, cf. Fig. 3, curve A.

All the fractions dominated by the 4 100-pigment were combined and rechromatographed, which only increased somewhat the depth of the minima in the longwaved band group. When the solvent was removed from these fractions, the residue crystallised immediately as yellow prisms of extreme instability. It was possible neither to obtain a m. p. determination nor to carry out ordinary weighings for spectral investigations as the 4 100-pigment turned into a black insoluble mass at room temperature in a few minutes.

The extinction coefficient of the U.V.-curve given in Fig. 1, curve A, is probably somewhat in error, since the removal of the solvent in a vacuum, in order to avoid decomposition, has not been carried out long enough to guarantee complete absence of solvent. The concentration of the infra-red spectrum, Fig. 2, curve A, is only approximative. The total substance used for the infra-red spectrum was afterwards used for the catalytical hydrogenation and the concentration is based on the weight of the perhydrocompound which, of course, was completely stable.

As long as the 4 100-pigment was handled in dilute solutions decomposition seemed to be rather slow. Since 2:6-dimethyl-octatetraene = cosmene had polymerised extensively in the infra-red cells in the course of the about 20 minutes necessary for a 2–15  $\mu$  run, we were rather surprised that the 4 100-pigment did not show any sign of decomposition during the course of the spectral measurements, as judged from a rerun of some of the first peaks.

This phenomenon: extreme instability as crystalline solid — fair stability in dilute solutions, has been described earlier in connection with synthetic poly-acetylenes and was most striking in the work of Celmer and Solomons<sup>9</sup> on the antibiotic mycomycin and its isomerisation product iso-mycomycin from *Nocardia acidophilus*.

It is an interesting question whether this extreme instability has some connection with the fact that this 4 100-pigment so far has been found in the different plants only in very small amounts, whereas the thermally rather stable diacetylenic compounds of the type matricaria ester, lachnophyllum ester and the esters of matricarianol often occur in remarkably high concentrations, 0.3–1 % of the fresh plant.

*Gnaphalium luteo-album* L.; seed sample Indian Botanic Garden, Sibpur, Calcutta, cultivated at Norges Tekniske Högskole 1953.

|               | g   | Ess. oil<br>‰  | U.V.-absorption                             |
|---------------|-----|----------------|---|
| Flowers       | 103 | 0.14           | Step out below 3 800 ÅU, no selective abs.  |
| Leaves & stem | 250 | 0.27           | » » » 3 400 » , » » » »                     |
| Roots         | 8.5 | 11.7 (extract) | maxima at 4 100, 3 790, 3 516, 2 860, 2 645 |

Chromatography on slightly deactivated alumina gave in the petroleum ether washings only material without selective absorption. The chromophore went in the 20 % benzene-petroleum ether eluates and was then conform with that of the 4 100-pigment. 50 % benzene and ethyl ether eluted further fractions with only broad and undistinct spectra.

*Gnaphalium silvaticum* L., collected at Lian near Trondheim, 1950.

|                           | g     | Ess. oil<br>‰ | U.V.-absorption                            |
|---------------------------|-------|---------------|--|
| Flowers, leaves and stems | 1 082 | 0.041         | step out below 3 400 ÅU, no selective abs. |
| Roots                     | 277   | 0.29          | maxima at 2 860, 2 650 ÅU                  |

*Blumea lacera* D. C., seed sample Indian Botanic Garden, Calcutta, cultivated in a greenhouse at Norges Tekniske Högskole 1953.

|                | g     | Ess. oil<br>‰ | U.V.-absorption   |
|----------------|-------|---------------|---|
| Flowers        | 49    | 1.1           | semisolid substance, step out below 3 500 ÅU                            |
| Leaves & stems | 1 680 | 2.2           | liquid, step out below 3 500 ÅU   |
| Roots          | 890   | 2.2           | (extract) 4 100-chromophore on general step out at shorter wave-lengths |

The root extract was chromatographed on alumina. The fractions eluted with petroleum ether were devoid of selective absorption. 20 % benzene in petroleum ether eluted a fraction (362 mg) with the pure spectrum of the 4 100-pigment, calculated content of (V) was 3 %. This fraction deposited yellow rods from petroleum ether solution. Since at that time the extreme instability of this pigment was unknown, the main part was lost by decomposition.

The eluates with 60 % benzene until pure benzene eluted another chromophore with very distinct peaks:

|                                   |       |       |       |       |       |          |
|-----------------------------------|-------|-------|-------|-------|-------|----------|
| $\lambda_{\max}$                  | 3 485 | 3 250 | 3 055 | 2 872 | 2 675 | 2 560 ÅU |
| $\Delta\nu_{\max} \cdot 10^{-12}$ |       | 62.3  | 58.9  | 62.6  |       |          |

The spacing between the maxima reveals that this chromophore is acetylenic. In fact the maxima observed come very close to those of the symmetrical dienetriyne class, first exemplified in nature by the "Centaur X"-hydrocarbons of N. Löfgren<sup>10, 11, 12</sup>; observed for:



|                  |       |       |       |       |       |       |          |
|------------------|-------|-------|-------|-------|-------|-------|----------|
| $\lambda_{\max}$ | 3 485 | 3 260 | 3 064 | 2 895 | 2 694 | 2 592 | — — — ÅU |
|------------------|-------|-------|-------|-------|-------|-------|----------|

The "Centaur X" hydrocarbons are eluted with petroleum ether alone or with a few % benzene; obviously the chromophore from *B. lacera* must contain some polar group. The amounts of substance was too small for further investigations.

*Blumea lacinata*, *D. C.*, seed sample Indian Botanic Garden, Calcutta, cultivated in a greenhouse at Norges Tekniske Högskole 1953.

|                | g   | Ess. oil<br>‰ |                |   |                     |  |  |  |  |
|----------------|-----|---------------|----------------|---|---------------------|--|--|--|--|
| Flowers        | 95  | 1.7           | step out below | 3 400 ÅU                                    | , no selective abs. |  |  |  |  |
| Leaves & stems | 900 | 0.4           | » » »          | 3 400 »                                     | , » » »             |  |  |  |  |
| Roots          | 360 | 1.4           | maxima at      | 3 780, 3 520, 3 300, 3 100, 2 860, 2 650 ÅU |                     |  |  |  |  |

The essential oil from the root was chromatographed as above. The 20 % benzene eluate gave a very clear spectrum of (V).

|         |        |        |        |        |        |        |        |          |
|---------|--------|--------|--------|--------|--------|--------|--------|----------|
| maxima: | 4 110, | 3 785, | 3 520, | 3 295, | 3 090, | 2 865, | 2 715, | 2 650 ÅU |
|---------|--------|--------|--------|--------|--------|--------|--------|----------|

The eluates with higher percentages of benzene and with ethyl ether gave broad and undistinct spectra.

*Pulicaria vulgaris Gaertn.*, seed sample University Garden, Aarhus, and Agricultural College, Budapest, cultivated at Norges Tekniske Högskole 1952.

The essential oil of *Pulicaria vulgaris Gaertn.* was investigated by one of us, Dagny Holme, in her graduate work 1951; in the oil from the roots and the leaves some sharp peaks were then observed at 3 778, 3 505, 3 287, 2 865 and 2 645 ÅU standing out on a general step out towards shorter wave-lengths. The concentration of the 4 100-pigment was so small that the first maximum was overlooked. The 1952-material was chromatographed in the way found convenient with *Helipterum* oils. The petroleum ether washings absorbed only below 2 600 ÅU. Eluates with 10 % benzene showed maxima at 4 103, 3 780, 3 520, 3 290 ÅU and a striking conformity with the curve for the crystalline 4 100-pigment.

Eluates with 20 % benzene showed broad and only rather weak absorption in the region of 3 300 ÅU. The more strongly adsorbed substances have so far not been investigated.

*Sanvitalia procumbens Lam.*; seed sample Olsens Enke No. 4 484, cultivated at Norges Tekniske Högskole 1952.

|                | g    | Ess. oil<br>‰ |                |          |                     |  |  |  |
|----------------|------|---------------|----------------|----------|---------------------|--|--|--|
| Flowers        | 47.5 | 0.46          | step out below | 3 500 ÅU | , no selective abs. |  |  |  |
| Leaves + stems | 179  | 0.21          | » » »          | 4 000 »  | , » » »             |  |  |  |

The essential oil from the roots, 70.8 mg = 0.44 ‰, was chromatographed on a small column of deactivated alumina. The petroleum ether washings were devoid of selective absorption in U.V., the eluate with 50 % benzene contained the 4 100-pigment, seemingly



without presence of other chromophores, observed maxima: 4 100, 3 780, 3 520, 3 190 and 2 865 ÅU.

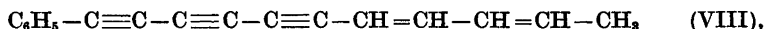
The column was then eluted with ethyl ether; this fraction had only a broad absorption band at 3 300 ÅU.

*Xanthium unknown sp.* Seed sample Abbot Co., cultivated at Norges Tekniske Högskole 1952. The plants did not develop flowers and thus a botanical determination was not possible.

|               | g      | Ess. oil<br>‰ |                                  |
|---------------|--------|---------------|----------------------------------|
| Leaves + stem | 14 000 | 0.04          | maxima at 3 670, 3 408, 3 100 ÅU |
| Roots         | 1 380  | 0.56          | maximum at 2 860 ÅU              |

The crude essential oil from the roots had a rather sharp peak in U.V. at 2 870 ÅU. The oil was chromatographed from petroleum ether followed with 50 % benzene-petroleum ether. The first 1/4 of the petroleum ether washings contained rather large amounts of colourless hydrocarbons without selective absorption in U.V. (terpenes?). The first washings with 50 % benzene contained the characteristic peaks of the 4 100-pigment. The solvent was evaporated and the fraction rechromatographed using elution with 8, 16, 25 and 50 % benzene in petroleum ether. The 25 % benzene eluates had a fair U.V.-spectrum of the 4 100-pigment. On evaporation of the solvent 1 mg of yellow crystals was left which immediately was dissolved in spectral hexane, U.V.-spectrum Fig. 3, curve B.

The essential oil from the leaves + stems were also chromatographed on alumina. The 10 % benzene in petroleum ether eluate had U.V. absorption close to that of 1-phenyl-*n*-undeca-7:9-diene-1:3:5-triène,



isolated recently from some *Coreopsis* species. Rechromatography brought the spectrum very close to that of (VIII). As the amount of pure substance isolated was very small only an infra-red spectrum could be taken, which was in good agreement with that of (VIII). Thus either (VIII) or a close relative of (VIII) must be present in *Xanthium* oils.

*Xanthium strumarium L.* Seed sample Indian Botanic Garden, Calcutta. A dozen plants of this rather tiny species were cultivated in a greenhouse at Norges Tekniske Högskole 1953. The male and female flowers were worked up separately, but neither of these oils showed any selective absorption in U.V. The essential oil from leaves and stems (16 ‰) had no selective abs.

The essential oil from the roots was chromatographed on alumina as above using 10 and 20 % benzene in petroleum ether as eluents.

The 20 % eluate contained the characteristic peaks of the 4 100 chromophore.

*Synedrella nudiflora Gaertn.* Seed sample Indian Botanic Garden. Cultivated in a greenhouse at Norges Tekniske Högskole 1953. This weed has very small flowers which were collected through the entire flowering season in order to obtain somewhat more material. The oil extracted with acetone showed, however, no selective absorption in U.V.

|                  | g   | Ess. oil<br>‰ |                           |
|------------------|-----|---------------|---------------------------|
| Leaves and stems | 564 | 0.4           | no selective abs. in U.V. |
| Roots            | 88  | 4.3           | maximum at 2 860 ÅU       |

The essential oil from the roots (0.38 g) was chromatographed on alumina. The petroleum ether washings were followed with 20 % benzene in petroleum ether, which eluted a fraction with U.V.-spectrum conform. with that of the 4 100-pigment.

Observed maxima: 4 110, 3 805, 3 515, 3 285 ÅU

*Acknowledgements.* Grants from *Norges Almenvitenskapelige Forskningsråd*, which have enabled these investigations to be carried out, are gratefully acknowledged.

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Received June 28, 1954.