The Carotenoids of Gagea lutea (L.) Ker-Gawl.

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Very little is known about the carotenoids of the plant family Liliaceae. Apart from an investigation of Narthecium ossifragum (L.) Huds.¹ it seems that only scattered and isolated finds have been reported. Lycopene has thus been shown to be present in Convallaria majalis L.,² rhodoxanthin in Haworthia coarctata var. kraussi Resende,³ and in Aloe vera L. and Bulbine annua (L.) Willd.⁴

In Narthecium 15 of the 22 carotenoids recorded were epoxidic in nature, according to the ether-hydrochloric acid test for 5,6-or 5,8-epoxides. Epoxidic carotenoids (antheraxanthin and violaxanthin) have also been reported from several Lilium species. ^{5,6} Other Liliaceae, viz. Tofieldia pusilla (Michx.) Pers. and Phormium tenax Forst., are rich in epoxidic carotenoids. (Unpublished results).

Gagea lutea (L.) Ker-Gawl. is another liliaceous plant in which epoxidic carotenoids are dominating, qualitatively as well as quantitatively. With the exception of fraction 10 (lutein), fraction 12 (probably cryptoxanthin), and fractions 13-15 (β -carotene, α -carotene, and phytofluene, respectively), all fractions listed in Table 1 gave a more or less pronounced blue colour when dissolved in ether and treated with hydrochloric acid.

The fractions 1 and 2 contained substances corresponding in their properties to neoxanthin and auroxanthin, respectively. The fractions 3 and 4 were relatively stable towards dilute acids, excluding the presence of 5,6-epoxides; the substances presumably were flavoxanthin and chrysanthemaxanthin, respectively. Fraction 5 displayed the spectrum of violaxanthin; on acid treatment it gave a substance corresponding to fraction 2. The zones 6-8 contained carotenoids displaying spectra of the auroxanthin (6-7) and flavoxanthin (8)types, however, these zones were much less strongly adsorbed to the columns than the auroxanthin and flavoxanthin in zones 2 and 3. Fraction 9 seemed to be lutein epoxide.

Experimental. Fresh plant material (inflorescences) of Gagea lutea (L.) Ker-Gawl., collected at Ås, Norway, was extracted with

Table 1. Carotenoids of Gagea lutea (L.) Ker-Gawl. Zones numbered in order of decreasing adsorptivity.

| Zone No. | Adsorption maxima, m μ . Solvent benzene | | | Tentative identification |
|----------|--|------------------|------------|--------------------------|
| | 478 | 447 | 420 | Neoxanthin |
| 2 | 435 | 408 | 385 | Auroxanthin |
| 3 | 458 | 430 | 407 | Flavoxanthin |
| 4 | 460 | 431 | 408 | Chrysanthemaxanthin |
| 5 | 484 | 453 | 425 | Violaxanthin |
| 6 | 435 | 409 | 388 | |
| 7 | 436 | 409 | 388 | |
| 8 | 459 | 433 | 410 | |
| 9 | 482 | 453 | 425 | Lutein epoxide |
| 10 | 487 | 457 | 432 | Lutein |
| 11 | 485 | 456 | 432 | |
| | Solve | ent petroleum et | ther | |
| 12 | 475 | 445 | 425 | Cryptoxanthin (?) |
| 13 | 477 | 448 | | β -Carotene |
| 14 | 475 | 447 | | α-Carotene |
| 15 | 368 | 348 | 330 | Phytofluene |

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cold acetone. The extracts were concentrated and the lipids transferred to peroxide free ether. After saponification with 10 % ethanolic potassium hydroxide, the carotenoids were partitioned between petroleum ether and 90 % methanol. After evaporation to dryness much colourless material was removed by dissolving in acetone and cooling to $-60^{\circ}\mathrm{C}$, when sterols and fatty alcohols precipitated and were filtered off. All operations were carried out in a nitrogen atmosphere.

The hypophasic carotenoids were chromatographed on columns of precipitated calcium carbonate (Riedel-de Haën) and developed with benzene. The epiphasic carotenoids were chromatographed on calcium hydroxide and developed with petroleum ether (b.r. 60 – 80°C). The individual zones were cut out and their absorption spectra measured on a Beckman DB recording spectrophotometer. The spectra were measured again, after the fractions had been rechromatographed on kieselgur-containing paper (xanthophylls) 7 or aluminium oxidecontaining paper (carotenes).8

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