

**Studies Related to Naturally Occurring Acetylene
Compounds. XVI. A conjugated Tetraene — Cosmene —
from the Essential Oil of *Cosmos bipinnatus***

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Recently Stavholt Baalsrud *et al.*¹ described in this journal the occurrence of a volatile polyene, b.p. $\sim 40^\circ$ at 0.3 mm Hg, present in small amounts in the essential oil of *Amellus strigosus* (Thunb.) Less. The absorption maxima in U. V. were given as:

3 091 2 959 2 822 and 2 300 (*cf.*¹ Fig. 3 p. 889)

By the spectroscopical investigations of a lot of new essential oils from plants belonging to the family of the *Compositae* cultivated at Norges Tekniske Högskole, Trondheim, in the summer 1952 this polyene was found to be present in at least the 9 following plants:

<i>Ambrosia trifida</i>	Root
<i>Amellus strigosus</i>	Leaves
<i>Ammobium alatum grandiflorum</i>	Leaves & root
<i>Coreopsis Drummondii</i>	Root
<i>Coreopsis verticillata</i>	Leaves & root
<i>Cosmos bipinnatus</i>	Flowers & leaves
<i>Felicia amelloides</i>	Leaves
<i>Helianthus annuus</i>	Leaves
<i>Pulicaria vulgaris</i>	Leaves

In most cases the polyene is found present only in very small amounts and its presence is realised only when the substance is concentrated by chromatography or fractionation, but in *Coreopsis verticillata* and especially in *Cosmos bipinnatus* (investigated in 4 different garden varieties: *Cosmos bipinnatus* "Sensation Rosenelfe", "*praecox grandiflorus*", "*praecox nanus roseus*", "Gloria rosa") a polyene with these characteristic maxima constitutes an appreciable part of the essential oil. These oils are good starting materials for this polyene; the steam distillation however, has to be carried out in a slow stream of pure nitrogen and with exclusion of light, because the polyene, when

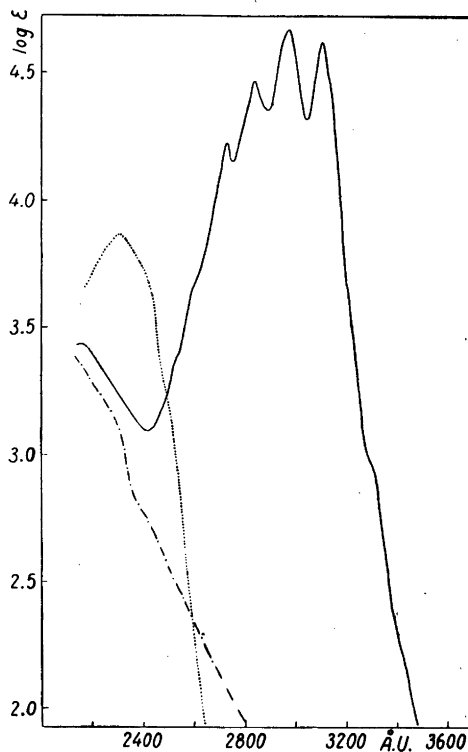


Fig. 1. Ultraviolet absorption in hexane of
 ——— cosmene m.p. -1°
 cosmene maleic acid anhydride
 mono adduct
 - - - - cosmene maleic acid anhydride
 mono adduct

present in higher concentrations, readily polymerizes to a white solid insoluble in ordinary organic solvents.

Cosmos bipinnatus gives reasonable yields of essential oil — $\sim 0.5\%$ — with high extinction coefficients and has been used in the experiments to elucidate the constitution. At 0.2 mm the main portion distills at $\sim 26^{\circ}$ as a liquid which is colourless in absence of oxygen and light.

Stavholt Baalsrud *et al.* suggested that this polyene chromophore belonged to a hydrocarbon on the basis of the remarkable volatility and the fact that this chromophore is only slightly retarded on activated alumina in petroleum ether solution. Combustion analysis on concentrates from *Cosmos bipinnatus* confirmed this supposition. Such concentrates are utterly unstable in air and very difficult to analyse but as C + H was found $> 98\%$ a substance with this volatility must obviously be a hydrocarbon.

The U.V. absorption maxima of this hydrocarbon — for which we propose the name *Cosmene* — are intermediate between octatetraene² and an ω, ω' -dialkyltetraene as for example parinaric acid³.

Octatetraene	λ_{\max} :	3 040	2 905	2 780	2 680
Cosmene	λ_{\max} :	3 097	2 960	2 830	2 720
Parinaric acid	λ_{\max} :	3 200	3 050	2 915	—

Cosmene thus might be a tetraene and it was tempting to try to obtain stable derivatives for analyses by addition of maleic anhydride.

Cosmene reacts readily with maleic anhydride at room temperature. Equimolecular amounts give a mixture of mono-adducts distilling at 90—95° at 0.0005 mm Hg as a viscous liquid. This monoadduct is obviously a mixture of isomers; the addition has to some extent taken part from the end of the tetraene system since the liquid monoadduct shows a single maximum at 2 300 ÅU, $\epsilon_{\max} = 7\,350$, Fig. 1. A disubstituted butadiene has $\lambda_{\max} = 2\,260$ and $\epsilon_{\max} = 21\,000$ — $22\,000^4$. The diene portion of the mono-adduct thus might be about 33 %. The liquid monoadduct does not give a quite satisfactory analysis, the found values falling between the calculated values for C_9H_{12} and $C_{10}H_{14}$ + one mole maleic anhydride. A diadduct is obtained in fair yield when cosmene is distilled directly into a frozen solution of benzene-maleic anhydride which then is slowly thawed. The cosmenediadduct is a crystalline solid, m.p. 198—199 with decomposition. The U.V.-absorption curve shows only a step out below 2 400 ÅU. Analysis of the crystalline diadduct agrees well with $C_{18}H_{18}O_6$ that is $C_{10}H_{14} + 2 C_4H_2O_3$.

Thus, cosmene is either a mono-ethyl- or a dimethyloctatetraene. From the infrared-spectrum we suppose that cosmene is 2 : 6-dimethyl-octatetraene. It was necessary to obtain cosmene in a state of reasonable purity before reliable conclusions could be drawn from the infrared spectrum, and it turned out to be very difficult to purify this tetraene. Our preliminary concentrates from *Cosmos bipinnatus* showed all of them the 2 300 ÅU max. in U.V., which was by far the strongest one in the *Amellus* fractions¹. In these concentrates the height of this 2 300-maximum was about the same as the 3 100—2 960 maxima. By repeated chromatography on alumina and distillation this 2 300 ÅU maximum was brought down about 1.0 in $\log E_{1\text{ cm}}^{\%}$ in relation to the 3 100—2 960 maxima. These concentrates solidified at -30° and a further purification could be achieved by crystallisation from petroleum ether at -70° . The m.p. of the first crystal fraction was -7 — -8° . Recrystallisation brought the m.p. to -1 — -2° which could not be raised any further. In the U.V. spectrum of these preparations the 2 300 maximum had completely disappeared, as will be seen from Fig. 1. The best preparations had a minimum at 2 390 ÅU followed by a step out at shorter wavelengths. The extinction coefficient of the 3 100—2 960 maxima increased some 60 % by this purification. The 2 300-chromophore might belong to a related hydrocarbon with a diene-grouping.

The purification was checked by infrared spectra in the 2—15 μ region. Besides an appreciable increase in the intensity of most of the main absorption maxima, the purification led to a gradual disappearance of not less than 9 maxima of medium intensity (1 650, 1 612, 1 278, 1 105, 978, 865, 830, 783, 755 cm^{-1}).

The infrared spectrum of our purest cosmene preparation is given in Fig. 2 together with the curve given by Forrest Woods and Schwartzman for octatetraene² redrawn to the same scale. Both spectra are dominated by maxima characteristic of olefins. A comparison of the infrared spectrum of cosmene with those of other known olefins and polyenes makes the following conclusions justified.

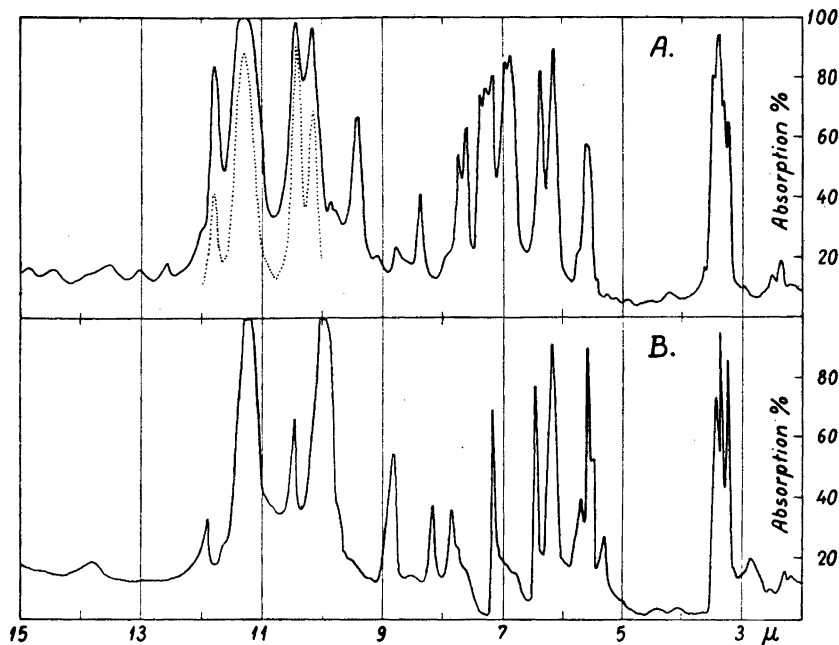


Fig. 2. Infrared absorption of

A: cosmene, liq., cell length ——— 0.025 mm 0.0125 mm
 B: octatetraene 1 : 3 : 5 : 7 in CS_2 soln. redrawn after ².

1. Cosmene shows the strong 1372 cm^{-1} band of the methyl group, which is lacking in the spectrum of octatetraene. Since there is no 770 cm^{-1} band — characteristic of an ethyl-group cosmene is obviously a dimethyl-octatetraene.

2. Cosmene shows a strong band at $958\text{--}960\text{ cm}^{-1}$. A band at an identical position is present in octatetraene. This region is typical ⁵ of the symmetrically substituted double bond $R-C=C-R'$ both in the *cis* and the *trans* form.



For isolated double bonds of this type the position $965\text{--}980\text{ cm}^{-1}$ is given; the slight displacement in octatetraene and cosmene is apparently due to conjugation. The *cis*-bond gives a strong peak in the $690\text{--}720\text{ cm}^{-1}$ region. Since cosmene shows only weak absorption in this region, the configuration must be *trans*.

The symmetrical *trans* double bond further gives a band of medium intensity at $1295\text{--}1310\text{ cm}^{-1}$; cosmene has a sharp peak at 1295 cm^{-1} .

3. The vinyl-group is characterized ⁵ by strong bands at 914 and $981\text{--}999$, medium bands at 1425 and 1825 cm^{-1} . Rasmussen *et al.*⁷ have shown that the 914 band of the vinyl group is displaced to $902\text{--}910$ in simple dienes. In 4-methyl-1:3-pentadiene⁸ this band lies at 894 cm^{-1} and in octatetraene² the position is at 898 cm^{-1} . The displacement of the 914 cm^{-1} band in dienes and polyenes cause this band to coalesce with the very strong $885\text{--}895$ band of

the methylene group ($\text{H}_2\text{C} = \text{C} \setminus$) if this grouping is present, *cf.* the spectra given by Sörm, Pliva *et al.* for myrcene and natural farnesene ^{9,10,11}.

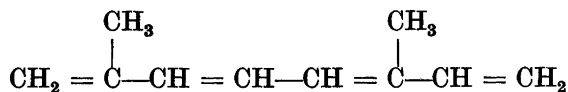
As is seen from Fig. 2 cosmene has a rather strong $1\ 787\ \text{cm}^{-1}$ band (octatetraene $1\ 805$, 4-methyl-1 : 3-pentadiene $1\ 790\ \text{cm}^{-1}$) a strong $986\ \text{cm}^{-1}$ band and a broad and strong band at $879\text{--}889$, the two first undoubtedly belong to the vinyl group, the last to the sum of the coalescing vinyl and methylene bands.

4. The $885\text{--}895\ \text{cm}^{-1}$ band of the methylene group is a very strong band and mostly very characteristic as it is little influenced by the rest of the molecule. The vinyl band in the $900\ \text{cm}^{-1}$ region is regularly weaker than the $994\ \text{cm}^{-1}$ band, as is seen from Fig. 2. Cosmene, however, has a much stronger and broader band at $879\text{--}889$ than at $986\ \text{cm}^{-1}$. There should be no doubt that the methylene group is present in cosmene.

Rasmussen *et al.*⁷ has further demonstrated that all compounds containing the $\text{H}_2\text{C} = \text{C}$ -group have bands between $1\ 640$ and $1\ 668\ \text{cm}^{-1}$. Cosmene has two sharp peaks at $1\ 572$ and $1\ 627\ \text{cm}^{-1}$; the corresponding peaks of octatetraene are found at $1\ 563$ and $1\ 636\ \text{cm}^{-1}$, and thus these band might belong to the conjugated vinylgroup.

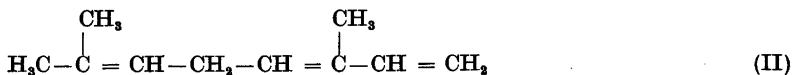
5. The tri-substituted double bond is characterized by a band of medium intensity in the $800\text{--}840\ \text{cm}^{-1}$ region, the position of which is rather influenced by surrounding groups. Cosmene has a sharp band of medium intensity at $847\ \text{cm}^{-1}$ which might belong to a trisubstituted double bond.

The infrared spectrum of cosmene thus rather distinctly indicates that this hydrocarbon contains all the types of double bonds present in 2 : 6-dimethylocta-1 : 3 : 5 : 7-tetraene (I).



Other formulations (as 2 : 3 and 2 : 4-dimethyloctatetraene) would also satisfy the data given above. The preliminary choice of I has of course been made while a constitution as a dehydrogenated aliphatic monoterpene might be the most probable one for a branched dimethyloctatetraene. That cosmene must be branched is evident from the infrared spectrum as well as from the fact that deca-2 : 4 : 6 : 8-tetraene is a known compound, m.p. 125° ¹².

The presence of ocimene (II) in the essential oil of *Tagetes glandulifera* has been demonstrated by Jones and Smith¹³.



This occurrence has recently been confirmed by Sutherland¹⁴, who established that the double bond position in ocimene is as in (II), in contrast to older work which preferred an isopropenyl end group. *Tagetes glandulifera* belongs to the plant family of the *Compositae*, *Tribus Helenieae*, which tribus is rather little investigated chemically. It is interesting to note that in no fraction of the investigated essential oils originating from *Cosmos*-species or the other 8 plants mentioned above we have found spectroscopic evidence for the presence of conjugated trienes. It thus looks as if ocimene is not isomerised to allo-ocimene, but only dehydrogenated to a tetraene = cosmene.

The aliphatic sesquiterpene analogue of myrcene, natural farnesene¹⁵, has been isolated from some plants belonging to the *Compositae*^{11,1}. It should be mentioned that the essential oil of *Felicia Bergeriana* (*Tribus Astereae*) contains an extremely unstable substance with U.V. absorption maxima close to those of a carotenoid hexaene:

Volatile chromophore in <i>Felicia Bergeriana</i>		λ_{\max} : 3 718 3 522 3 359				\AA U (in Hexane)	
$\Delta\nu \times 10^{-12}$		44.9		41.3			
2 : 4 : 6 : 8 : 10 : 12-Tetradecaheptaene ¹²	»	3 750	3 600	3 400	3 280	»	(» CHCl_3)
ω,ω' -Dihydrocroetin ¹⁶	»	3 790	3 600	3 400		»	(» alcohol)
Anhydro-vitamin-A ₁ ²⁴	»	3 900	3 700	3 500		»	»
<i>iso</i> Anhydro-vitamin A ₁ ²⁴	»	3 700	3 500	3 300		»	»

The hexaenic chromophore is present only in small amounts, and an isolation from natural sources would be rather futile if another much richer source of this polyene cannot be found. It would, however, be very interesting to learn if this hexaene were the sesquiterpene analogue of cosmene, that is tetradehydro-natural-farnesene. Thus with cosmene the dehydrogenated type of terpenes, so far characteristic of the tetraterpene class, is demonstrated for the first time as a natural product in the simplest of all terpenes, and the occurrence of this type in other terpenes is of general interest. It has to be remembered that it is the property of the carotenoids to be pigments and mostly rather stable solids with high crystallising power, which has made possible the isolation and elucidation of structure of this dehydrogenated class of compounds. Very unstable colourless liquid compounds occurring in the same low concentrations have very little chance to be discovered and isolated. The difficulties met with in the hydrogenated carotenoids phytofluene and phytoene are typical of the situation^{17,18}. Whilst these hydrogenated carotenoids have chromophores with from 4 to 6 conjugated double bonds, it is worth while to remember that the same chromophores might belong to conjugated mono- and sesquiterpenes.

From alcoholic extracts of different *Centaurea*-species Löfgren^{19,20} isolated, besides acetylenic hydrocarbons — the Centaur X hydrocarbons — some polyenes supposed to be tetraenes — the Centaur Y hydrocarbons. The U.V.-maxima of the Centaur Y-hydrocarbons are displaced some 80–98 \AA U relative to cosmene:

Centaur Y ₁ and Y ₂	3 195	3 045	2 915	2 800	\AA U
Cosmene	3 097	2 960	2 830	2 720	»

and so approaches the maxima of parinaric acid. We have so far not met the maxima of Centaur Y in any of our essential oils.

Centaurea also belongs to the *Compositae* family, tribus *Cynareae*. We have investigated some other members of this tribus, which seems to be very rich in acetylenic compounds and we have found some compounds, which, to judge from the frequency differences of the maxima, are polyenic. The spectral curves of the crude chromatographic fractions seem, however, to indicate aromatic compounds. The composition of these essential oils will be dealt with at a later occasion. So far the Centaur Y hydrocarbons seem to be restricted to the genus *Centaurea*.

EXPERIMENTAL

When preliminary experiments showed that the flowering and the green parts and the roots of the 4 different garden varieties of *Cosmos bipinnatus* gave essential oils with the same U.V.-spectra, the main plant material was steam distilled without separation in a 100 liter pan. When distilled without any precautions being taken, the essential oil at once polymerised into solid flakes swimming on the condensate; the main distillation was carried out with exclusion of light and in an atmosphere of pure nitrogen. All samples were stored in the cold with addition of a little hydroquinone and redistilled immediately before use. Yield of essential oil: flowers 2 %, leaves + stems 0.7 %, roots 0.4 %; cosmene concentration in the oil 20–40 %.

We have not succeeded in a purification of cosmene by fractional distillation alone. At 10 mm heating to the temperature necessary for distillation caused polymerisation of

most of the cosmene; at 0.3 mm the separation was unsatisfactory. The fractions boiling at about 30°/0.3 mm were combined and chromatographed on deactivated alumina²¹ from petroleum ether solution and the chromatogram developed with further washings with petroleum ether. Portions of the filtrate were examined on their U.V.-absorption. Cosmene was only slightly retarded, slightly yellow zones in the chromatogram facilitate the separation of fractions. The fractions richest in the tetraene chromophore were combined, distilled and crystallised from petroleum ether at -70°. Since cosmene was very soluble in petroleum ether below zero the separation of the voluminous crystals was difficult. The best results were obtained with a diver with a glass filter which removed most of the solvent at -70° leaving a cake of solid cosmene on the filter. To remove the solvent this cosmene was redistilled, m.p. -2° - -1°. Infrared spectrum, compare Fig. 2 U.V. spectrum, compare Fig. 1.

ϵ_{\max}	42 750	47 500	30 000	16 900	ÅU
λ_{\max}	3 100	2 965	2 838	2 730	ÅU
$\Delta\nu_{\max} \times 10^{-12}$		44.1	45.3	41.8	

Cosmene was too unstable for refractional measurements at ordinary temperature. The best fraction of cosmene gave immediately after redistillation, $n_D^{20} = 1.584$

<i>cf.</i> allo-ocimene	$n_D^{25} = 1.5420$ ²²
ocimene	$n_D^{25} = 1.4890$ ²²
myrcene	$n_D^{21} = 1.4700$ ²³

As will be seen, the rise in conjugation from the conjugated dienes of the normal aliphatic terpenes to the trienoid and tetraenoid relatives increases the refraction index about 0.04-0.05.

Cosmene maleic anhydride mono adduct. 0.33 g of cosmene and 0.27 g of freshly distilled maleic anhydride in benzene solution was left at room temperature for 3 hours. The solvent was evaporated and the reaction mixture distilled at 0.0005 mm. Some unreacted anhydride went into the trap, and a viscous colourless oil passed over at air bath temperature 90-95°.

	Found	C 71.35, 71.28;	H 7.64, 7.58
$C_{10}H_{14} + C_4H_2O_3$	calc.	» 72.37;	» 6.95.
$C_9H_{12} + C_4H_2O_3$	calc.	» 71.32;	» 6.47.

This liquid mixture of monoadducts could not be induced to crystallise, U.V.-spectrum in Fig. 1.

Cosmene-maleic anhydride diadduct. 0.40 g of cosmene was distilled at 0.3 mm directly into a trap containing 1.5 g of maleic anhydride in frozen benzene. The trap was slowly thawed and pure nitrogen let in only when the reaction mixture was liquid. Left under pure nitrogen for 12 hours. Worked up as above but the high vacuum distillation was interrupted at 90°. The excess maleic anhydride then was in the trap with small amounts of liquid in the receiver; the residue was solid. This residue was crystallised twice from acetone - petroleum ether. M.p. 198-199°.

$C_{10}H_{14} + 2 C_4H_2O_3 = C_{18}H_{18}O_6$	Calc.	C 65.43;	H 5.50.
	Found	» 65.53;	» 5.84.

SUMMARY

In the essential oils of a dozen plants belonging to the *Compositae* there has been found a tetraene chromophore. All parts of *Cosmos bipinnatus* are rather rich in this compound which turned out to be a hydrocarbon of m.p. -1°, "Cosmene". Through a maleic anhydride diadduct the composition could be established to be $C_{10}H_{14}$; infrared studies established the structure as one of three dimethyl-octatetraenes. Of these possibilities the 2:6-dimethyl-octatetraene structure is tentatively chosen in analogy with normal aliphatic terpenes.

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