Hydrocarbons and Other Weakly Polar Unsaponifiables in Some Vegetable Oils

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ABSTRACT

The hydrocarbon fractions obtained from sunflower, olive, soybean, rapeseed and pumpkin seed oils by fractionation of unsaponifiable matter were composed of n-paraffins, isoprenoidal polyolefins, squalene, diterpene and triterpene hydrocarbons and compounds with oxygen. Iso-, anteiso- and other branched hydrocarbons were not identified in any of investigated oils. Possible compounds with oxygen are aliphatic and alicyclic ketones, conjugated steroid ketones, esters and lactones. The differences in the hydrocarbon fractions of investigated oils suggest they may be used for characterization.

INTRODUCTION

Hydrocarbons represent the least investigated fraction of unsaponifiable matter of vegetable oils. Jacini and Fedeli (1) concluded that it was comprised of squalene, n-,iso- and probably anteiso-paraffins, and in some cases olefins. Capella et al. (2) established the presence of three groups of hydrocarbons: n-paraffins, iso- and/or anteiso-paraffins and olefins. In the n-paraffin series, they identified the members from n-C_{10} to n-C_{35}, whereas only iso- and anteiso-paraffins were identified in a small number of cases. The presence of small amounts of olefins was based on iodine values. Comparing the composition of hydrocarbons in a number of vegetable oils, these authors have concluded that oil is much less characterized by the hydrocarbon fraction than by other fractions, for example, those of triterpene alcohols. Hydrocarbons from soybean oil were among the first examined. Donia and Draken (3) identified in soybeans n-$C_{31}H_{64}$ as one of the main components of hydrocarbon fraction, and Yamada (4) identified also n-paraffins C_{28}, C_{29}, C_{30} and C_{32}. In sunflower oil, Jasperson and Jones (5) found hydrocarbons C_{20} and C_{30}. Eisner et al. (6) found that in olive oil squalene comprised about 85-90% of hydrocarbon fractions. The rest were normal chain, iso- and/or anteiso- and multiple branched chain hydrocarbons in the range C_{16}-C_{36}. In coconut oil Moura Fe et al. (7) identified n-paraffins from C_{17} to C_{32}. At the same time they established the presence of smaller amounts of iso-and anteiso-hydrocarbons, some other branched chain hydrocarbons and squalene. In the hydrocarbon fraction of rapeseed oil, Rutkowski et al. (8) found 36 components ranging between n-C_{11} and n-C_{31}. Walbecq (9) was among the first who examined the hydrocarbon fraction by means of capillary GLC column. In the peanut oil, he found more than 100 components, the paraffins from n-C_{11} to n-C_{35} squalene being the predominant one. Mordret (10) has established that hydrocarbon n-C_{29} (74.3% of the hydrocarbon fraction) was the main component in rapeseed oil. This hydrocarbon was present in considerable amounts in soybean and sunflower oils as well (19.6% and 32.4%, respectively). In addition these two oils contain also higher amounts of n-C_{31} (52.6% and 34.2%, respectively). The content of individual hydrocarbons in oil was quantitatively determined only in a few cases (6,7,9,10). Iso-, anteiso-, and branched chain hydrocarbons were identified usually by comparative GLC retention times against standards and by way of plots of retention times vs. equivalent carbon numbers. Therefore, their structures were considered as tentative. Limited data on the content and composition of hydrocarbons in vegetable oils, their significant role in the biosynthesis of other oil components, and an open question whether their composition and content represent a "finger print" of each particular oil, induced us to examine the hydrocarbon fractions from sunflower, olive, soybean, rapeseed and pumpkin seed oils.

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EXPERIMENTAL PROCEDURES

Material

Crude, unrefined rapeseed oil obtained by pressing from East Slavonia, Yugoslavia, production of 1974. Crude, unrefined olive oil obtained from Korčula island, "Lastovka" sort from Blato and Vela Luka, Yugoslavia, production of February, 1975. Crude, unrefined pumpkin seed oil obtained from the surroundings of Koprivnica, Yugoslavia, production of 1974. Crude, unrefined sunflower oil originating from Banat, Yugoslavia, production of 1975. Oil of soybeans from the surroundings of Lazarevac, Yugoslavia, obtained by extraction in laboratory conditions.

Standards of hydrocarbons from n-C_{10} to n-C_{32} and squalene were products of Koch-Light and Fluka firms.

The solvents were washed and dryed in the usual way (11) and finally distilled through a 600mm x 8mm column with "Heli-pak" packing.

Separation of Hydrocarbon Fraction

The unsaponifiable matter of oil was obtained by saponification and extraction with diethylether (12), which was afterwards removed under nitrogen on a water bath. Thin layer chromatography on Silica Gel G with alkaline modification (13) was used for the separation of unsaponifiable matter of oil. Separation was performed on 20x20cm plates, Silica Gel G of 0.5-1mm in thickness, by means of hexane-diethyl-ether mixture (1:1). The hydrocarbon band was identified by comparison with a mixture C_{22}, C_{24}, C_{26}, C_{28} and C_{32} hydrocarbon standards, and by spraying with 2,7-dichlorofluoresceine and observation under UV light. The hydrocarbon band was then removed from the plate, extracted with ether, evaporated under nitrogen, and the residue analysed by GLC.

Gas Liquid Chromatography

All TLC fractions were analysed on the Varian 1400 gas chromatograph equipped with a flame ionization detector on 1.5m x 4mm ID silanized glass columns, packed with 3% OV-17 and 1% OV-1 on 80/100 mesh Chromosorb W, and temperature programmed at 4 C/min from 125-265 C. Nitrogen was used as carrier gas. Glass capillary column GLC of the TLC fractions was performed on a Carlo-Erba 2101 AC instrument with a flame ionization detector and fitted with a 40 m x 0.3 mm ID column coated with SE-30. Operating conditions were: injection port 280 C;

TABLE I

Contents of Unsaponifiable and Hydrocarbons

Oils	unsaponifiable in % of oil	hydrocarbon in % of unsapon.	hydrocarbon in % of oil
rapeseed	0.98	19	0.18
olive	1.54	65	1.0
sunflower	0.79	13	0.10
pumpkin seed	1.06	50	0.53
soybean	1.38	28	0.38

temperature programmed 3 C/min from 150 to 300 C; helium carrier gas, 1.5 ml/min; hydrogen flow, 10 ml/min; air flow, 30 ml/min. Comparison with chromatogram obtained using a packed column indicated that no degradation of the sample occured in capillary column.

Combined Gas Chromatography – Mass Spectrometer – Computer

Analyses of TLC fractions were performed on the LKB 2091 gas chromatograph-mass spectrometer combination (GC-MS) equipped with LKB 2130 computer system. The gas chromatograph was fitted with a 30m x 0.3mm ID glass capillary column, coated with SE-30. Working conditions: temperature programmed 2 C/min from 150 to 300 C, carrier gas He, ionization source 275 C, ionization voltage 70 eV, total ionic current 20 eV.

Hydrogenation of the hydrocarbon fraction was performed in chloroform/acetic acid over PtO_2 catalyst in hydrogen atmosphere. The structure of the components in hydrocarbon fraction was determined by comparison of their mass spectra with those of authentic samples and published data. In few cases where this was not possible, the structure is given on the basis of information obtained from mass spectra. In the cases where molecular formulas were given they were determined by peak-matching in relation to PFK. The structure of n-paraffins was determined by comparison with mass spectra and methylene indices of authentic samples. Fatty acids ethyl esters were identified on the basis of their mass spectra. The identification of other compounds was accomplished as described in the following text. For each compound its methylene indices were calculated, but no attempt was made at quantitation. Methylene indices are given in parentheses in the text under figures. They are determined graphically on the basis of retention by linear interpolation between the values for neighboring n-paraffins.

RESULTS

The content of unsaponifiable matter of oil and the content of hydrocarbon fraction in unsaponifiable matter and in oil are presented in Table I.

Hydrocarbon Fraction of Rapeseed Oil

Figure 1 shows the gas chromatogram of TLC fraction obtained on the capillary column (40m).

Peak 8 is a compound which has an identical mass spectrum as hexahydrofarnesylacetone (14). It was found in the hydrocarbon fraction of other investigated oils.

Peak 10 is compound with molecular formula $C_{20}H_{36}$, which suggests a tricyclic diterpene structure. It shows the following mass spectrum (only fragments with relative intensities greater than 10% are given): m/e – 276 (30%, $C_{20}H_{36}$, M^+), 261 (19%), 247 (74%), 191 (51%), 165 (17%), 163 (76%), 151 (22%), 137 (45%), 135 (14%), 123 (80%), 121 (21%), 111 (20%), 109 (64%), 107 (21%), 97 (40%), 95 (81%), 93 (23%), 91 (20%), 83 (60%), 81 (86%), 79 (22%), 71 (17%), 69 (86%), 67 (52%), 57 (35%), 55 (100%), 43 (45%), 41 (98%). The great intensity of M-29

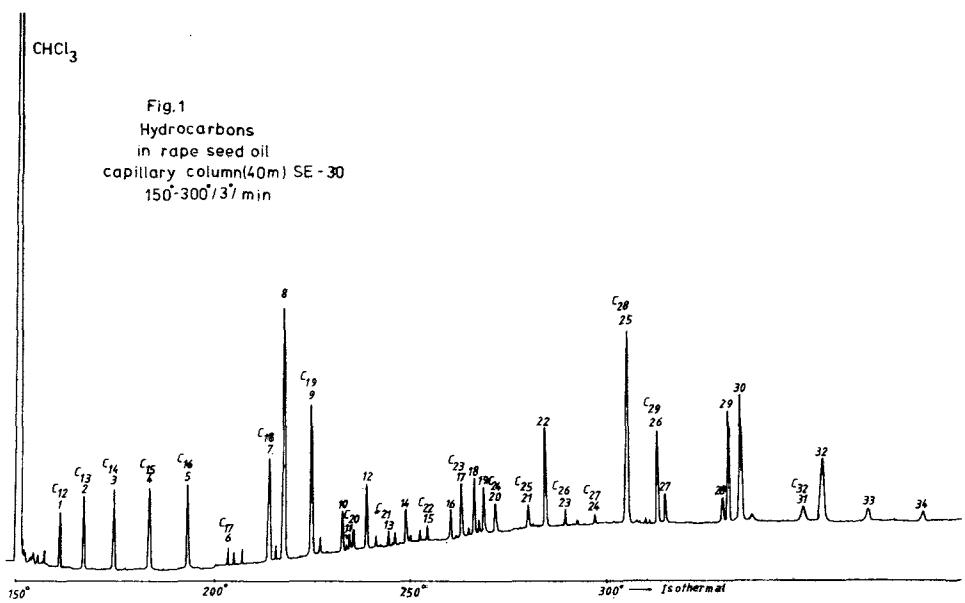


FIG. 1. Gas chromatogram of hydrocarbon fraction of rapeseed oil: 8. Hexahydrofarnesylacetone (18.40); 10. Diterpene $C_{20}H_{36}$ (19.65); 12. Diterpene $C_{20}H_{34}$ (20.35); 14. Ethyl ester oleic acid (21.45); 16. 4,8,12,16-tetramethylheptadecanone-2 (22.55); 18. unidentified lactone (23.40); 19. Ethyl ester eicosanoic acid (23.60); 22. Ethyl ester erucic acid (25.45); 27. Isoprenoidal polyolefin (29.15); 28. unidentified compound (30.65); 29. 2,6,10,14,18,22-hexamethyl-tricosanone-12 (30.70); 30. unidentified compound $C_{29}H_{50}O_2$ (30.85); 32. 24-methyl-$\Delta^{3,5,22}$-cholestatriene-7-one; 33. 24-methyl-$\Delta^{3,5}$-cholestadiene-7-one; 34. $\Delta^{3,5}$-sitostadiene-7-one.

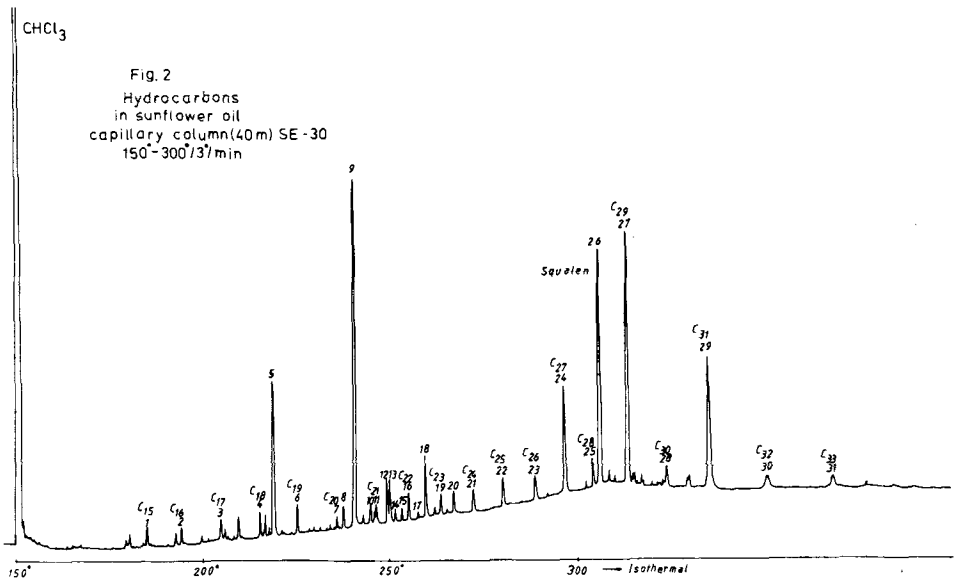


FIG. 2. Gas chromatogram of hydrocarbon fraction of sunflower oil: 5. hexahydrofarnesylacetone (18.40); 8. ethyl ester palmitic acid (20.15); 9. kaurene (20.40); 10. 7,11,15-trimethylhexadecanone-2 (20.85); 12. ethyl ester linoleic acid (21.30); 13. ethyl ester oleic acid (21.40); 14. ethyl ester stearic acid (21.50); 15. cyclic diterpeneketone (21.75); 17. isoprenoidal polyolefin (22.25); 18. 4,8,12,16-tetramethylhepta-decanone-2 (22.55); 20. unidentified lactone (23.40); 26. squalene (28.20).

fragment (74%) shows the presence of an ethyl group probably on a quaternary C-atom as in pimarane or some of its tricyclic isomers.

Peak 12 is a compound with molecular formula $C_{20}H_{34}$. It showed the following mass spectrum (above m/e 150 only fragments with relative intensities greater than 5% are given; in the range between m/e 100 and m/e 150 only fragments with relative intensities greater than 15% are given; under m/e 100, only fragments with relative intensities greater than 40% are given): m/e – 274 (38%, $C_{20}H_{34}$, M^+), 259 (32%), 245 (5%), 231 (18%), 189 (18%), 163 (11%), 150 (20%), 149 (18%), 148 (17%), 138 (17%), 137 (22%), 136 (30%), 125 (22%), 123 (100%), 121 (30%), 109 (41%), 107 (26%), 105 (13%), 95 (56%), 81 (65%), 69 (65%), 67 (43%), 55 (47%), 41 (60%). The molecular formula and the fragmentation pattern suggest the structure of a cyclic diterpene.

Peak 16 is a compound with the following mass spectrum (under m/e 200 only fragments with relative intensities greater than 10% are given): m/e – 310 (4%, M^+), 295 (2%), 292 (2%), 267 (1%), 252 (2%), 250 (3%), 96 (11%), 85 (14%), 83 (12%), 71 (46%), 69 (20%), 59 (76%), 58 (100%), 57 (26%), 55 (25%), 43 (77%), 41 (24%). The high intensity of the fragment m/e 58 (100%) and the lack of other fragments of higher intensity above m/e 100 as well as similarity to the mass spectrum of hexahydrofarnesylacetone suggest peak 16 as an alkylacetone of the following structure: 4,8,12,16 – tetramethylheptadecanone-2. This compound is present in the sunflower oil as well.

Peak 18 is a compound with the following mass spectrum (under m/e 250 only fragments with relative intensities greater than 20% are given): m/e – 292 (20%, M^+), 250 (8%), 111 (22%), 99 (100%), 97 (43%), 84(30%), 83 (44%), 81 (22%), 71 (26%), 69 (81%), 67 (28%), 57 (40%), 55 (98%), 43 (67%), 41 (65%). The fragment m/e 99 (100%) is typical for six-member lactones (15). This compound is present in sunflower oil.

Peak 27 is isoprenoidal polyolefin with molecular weight M=408. The identical compound is found in olive and pumpkin seed oils. More details on its structure are given in connection with hydrocarbons of olive oil.

Mass spectrum of peak 28 was of poor quality and inadequate for interpretation.

Peak 29 is a compound with molecular formula $C_{29}H_{58}O$. It showed the following mass spectrum (above m/e 180 all fragments present in spectrum are given; under m/e 180 only fragments with relative intensities greater than 10% are given): m/e – 422 (5%, $C_{29}H_{58}$ O, M^+ 407 (2%), 404 (2%), 379 (2%), 309 (3%), 267 (4%), 253 (12%), 241 (43%, $C_{16}H_{33}O$), 240 (28%), 225 (90%), 222 (7%), 211 (3%), 197 (4%), 182 (7%), 180 (16%), 127 (10%), 109 (12%), 97 (18%), 96 (22%), 95 (20%), 85 (35%), 83 (24%), 82 (23%), 81 (18%), 71 (93%), 69 (31%). 59 (43%), 58 (75%), 57 (100%), 55 (50%), 43 (97%), 41 (31%). The high intensity of fragment m/e 58 (75%), suggests a ketone, and the fragment m/e 225 (90%) strongly supports a ketone with two identical alkyl groups $C_{14}H_{29}$. The mass spectrum under 180 is similar to the mass spectrum of hexyhydrofarnesylacetone which shows that $C_{14}H_{29}$ group has the same carbon skeleton as farnesane. Therefore, peak 29 is interpreted as 2,6,10,14,18,22-hexamethyltricosanone-12.

Peak 30 showed following mass spectrum (above m/e 200 all fragments present in spectrum are given; in the range between m/e 130 and m/e 200 only fragments with relative intensities greater than 5% are given; under m/e 130 only fragments with relative intensities greater than 20% are given): m/e – 430 (14%), $C_{29}H_{50}O_2$, M^+), 241 (12%), 227 (50%, $C_{15}H_{31}O$), 225 (5%), 213 (11%), 165 (20%), 164 (7%), 153 (6%), 139 (12%), 125 (26%), 111 (53%), 97 (92%), 85 (33%), 83 (95%), 71 (53%), 69 (76%), 57 (100%), 55 (58%), 43 (82%), 41 (31%). The above data suggest peak 30 as either a polycyclic lactone or diketone.

From the mass spectrum, peak 34 was identified as $\Delta^{3,5}$-sitostadiene-7-one (16).

Peaks 32 and 33 have the following molecular weights: M=394 and M=396, respectively. Also mass fragmentations at m/e 161, 174 and 187 characteristic of a $\Delta^{3,5}$-7-keto steroid structure (17). On the basis of this and other fragments, these compounds were identified as 24-methyl-$\Delta^{3,5,22}$-cholestatriene-7-one and 24-methyl- $\Delta^{3,5}$-cholestadiene-7-one (18).

It is possible that these three steroid ketones were the products of dehydration of respective 3β-hydroxy-7-ketosterols which took place during the saponification. They are probably the oxidation product of brassicasterol, campesterol and β-sitosterol, which are the main compon-

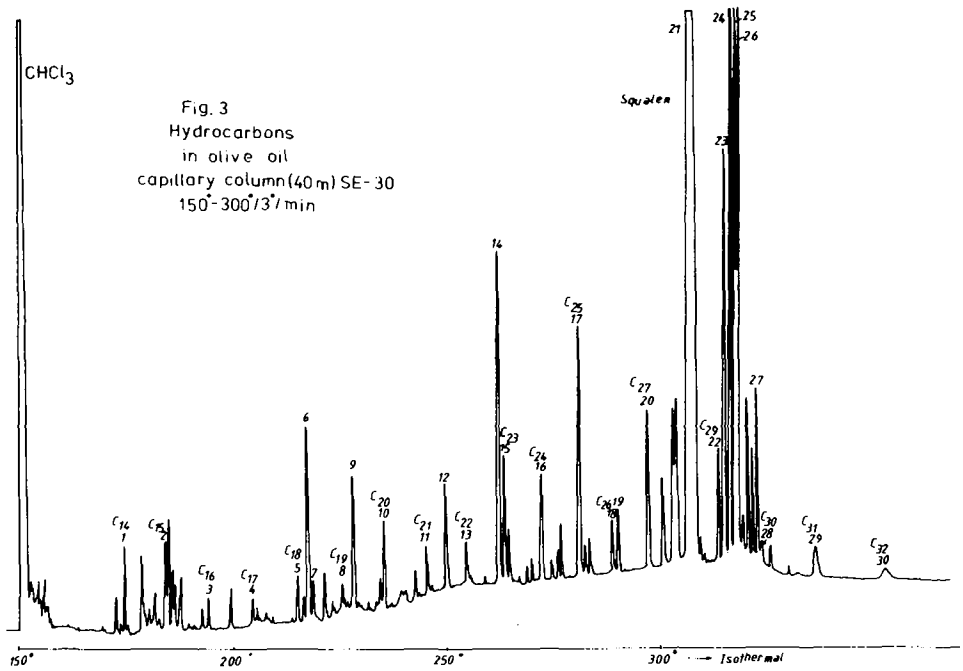


FIG. 3. Gas chromatogram of hydrocarbon fraction of olive oil: 6. IP[a] (18.25); 7. hexahydrofarnesylacetone (18.40); 9. IP (19.25); 12. IP (21.45); 14. (22.80); 19. IP (26.20); 21. squalene (28.20); 23. IP (29.15); 24. IP (29.20); 25. IP (29.25); 26. IP (29.30); 27.IP (29.95). [a]IP = isoprenoidal polyolefin.

ents of the sterol fraction of rapeseed oil (19). The oxidation could not take place during our treatment of rapeseed oil, because the same procedure performed on the sunflower oil which contains exceptionally high amount of β-sitosterol left no trace of a 7-keto-product.

Hydrocarbon Fraction of Sunflower Oil

Figure 2 shows the gas chromatogram of TLC fraction obtained on the capillary column (40m).

Peak 9 is a compound which was identified as kaurene on the basis of identical mass spectra with published data (20). It is also present in the pumpkin seed oil.

Peak 10 has the following mass spectrum (above m/e 200 all peaks present in the spectrum are given; under m/e 200 only fragments with relative intensities greater than 10% are given): m/e – 282 (5%, M^+), 267 (2%), 264 (2%), 224 (4%), 85 (15%), 83 (12%), 71 (39%), 69 (13%), 59 (73%), 58 (100%), 57 (23%), 55 (22%), 43 (76%), 41 (27%). The great intensity of the fragment m/e 58 (100%) and the lack of other fragments of higher intensities as well as the similarity to the mass spectrum of hexahydrofarnesylacetone, suggest an alkylacetone with the structure of 7,11,15-trimethylhexadecanone-2.

Peak 15 is a compound with the following mass spectrum (above m/e 200 only fragments with relative intensities greater than 10% are given; under m/e 200 only fragments with relative intensities greater than 20% are given): m/e – 286 (43%, $C_{20}H_{30}O$, M^+), 271 (16%), 257 (37%), 253 (10%), 243 (72%), 225 (21%), 215 (17%), 199 (23%), 187 (38%), 161 (36%), 147 (35%), 135 (28%), 133 (42%), 131 (40%), 123 (98%), 121 (23%), 119 (37%), 117 (28%), 109 (67%), 107 (57%), 105 (59%), 97 (38%), 95 (64%), 93 (61%), 91 (98%), 83 (27%), 81 (100%), 79 (82%), 77 (46%), 71 (40%), 69 (53%), 68 (35%), 67 (72%), On the basis of the fragmentation pattern, it is a cyclic diterpeneketone.

Peak 17 is isoprenoidal polyolefin with 22 C atoms. This compound will be explained in more details in connection with hydrocarbons of olive oil.

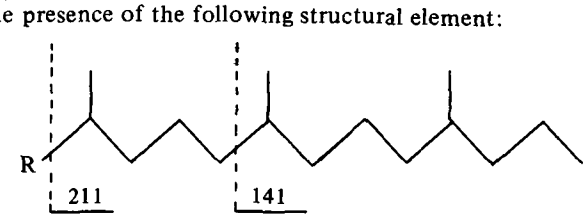
Peaks 18 and 20 have identical mass spectra and methylene indices to those of peaks 16 and 18 in rapeseed oil, which are already discussed.

Hydrocarbon Fraction of Olive Oil

Figure 3 represents the gas chromatogram of TLC fraction obtained on the capillary column (40m).

Peaks 6,9,12,14 and 19 are compounds with close similarity of their mass spectra, which have as the base peak ion of mass 69 and the fragments typical for mass spectrum of squalene (m/e 81, 95, 109, 123, 136, 137). They are probably isoprenoidal polyolefins with 18, 19, 21, 23 and 26 C atoms (M^+ 248, 262, 290, 316 and 356).

Peaks 23, 24, 25 and 26 represent compounds of molecular weight 408, with close similarity of their mass spectra, which in addition to molecular ions (M^+ 408 instead of 410), differ from the spectrum of squalene, first of all, by higher intensity of ions of mass 135 and 203, and by the presence of ions of mass 339 instead of 341, 271 instead of 273, and 229 instead of 231. In addition the relation is changed in the favor of lighter fragment in the mass pairs 189/191, 135/137, 107/109 and 93/95. The four isomeric compounds of molecular mass 408 can differ one from another by the position of double bonds as well as by the manner of binding of C-atoms. To clarify this the hydrocarbon fraction was hydrogenated. The gas chromatogram of the product showed 4 peaks of saturated hydrocarbons positioned after the peak of squalane and in similar quantitative ratios as in unhydrogenated sample. This proved the peaks 23,24,25 and 26 represent isomers with different carbon skeletons. For instance, the mass spectrum of one hydrogenated product is characterized by high intensity of ions of mass 141 and 211, which points at the presence of the following structural element:



Peak 27 is an isoprenoidal polyolefin having also the

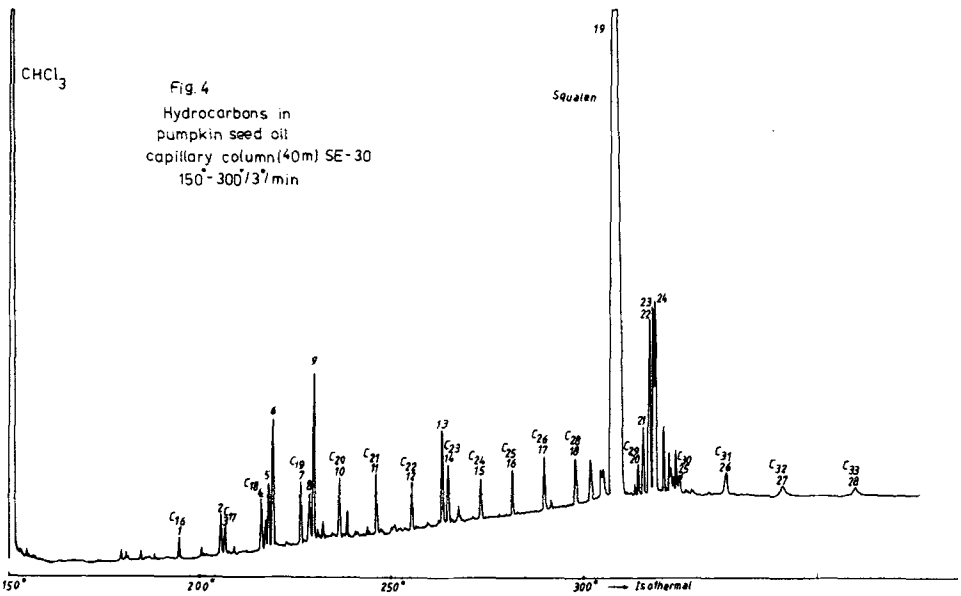


FIG. 4. Gas chromatogram of hydrocarbon fraction of pumpkin seed oil: 2. unidentified compound (16.90); 5. IP[a] (18.25); 6. hexahydrofarnesylacetone (18.40); 8. IP (19.25); 9. kaurene (19.40); 13. IP (22.85); 19. squalene (28.20); 21. IP (29.15); 22. IP (29.20; 23. IP (29.25); 24. IP (29.30). [a]IP = isoprenoidal polyolefin.

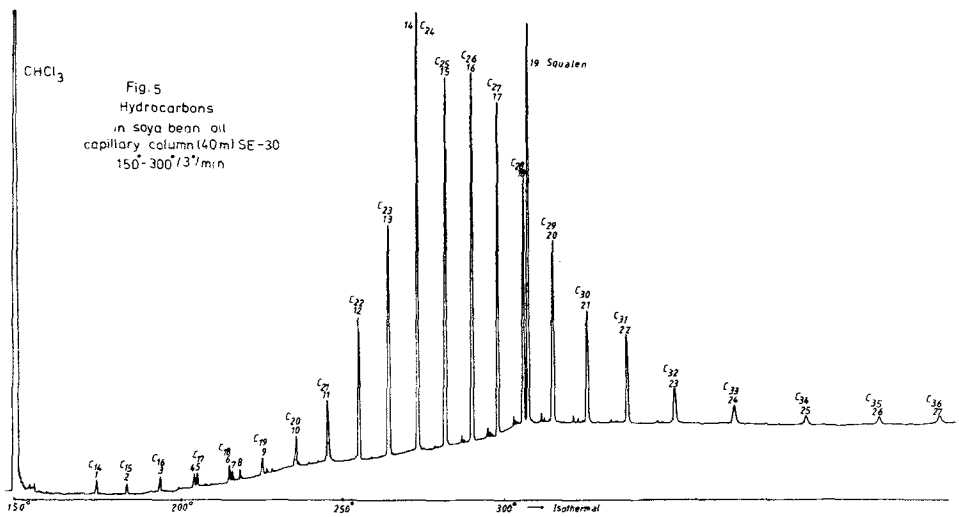


FIG. 5. Gas chromatogram of hydrocarbon fraction of soybean oil: 4. unidentified compound (16.95); 7. unidentified compound (18.15); 8. hexahydrofarnesylacetone (18.40); 19. squalene (28.20).

molecular weight 408. Its higher retention time than in other isomers with mass 408, suggests that it contains more nonbranched carbon chains (21).

Hydrocarbon Fraction of Pumpkin Seed Oil

Figure 4 represents the gas chromatogram of TLC fraction obtained on the capillary column (40m).

Peaks 5,8,13,21,22,23 and 24 have the same mass spectra and methylene indices as peaks 6,9,14,21,23,24 and 26 in the hydrocarbon fraction of the olive oil, where more details on their structure are given. Other compounds present are n-paraffins and compounds which have already been mentioned.

Hydrocarbon Fraction of Soybean Oil

Figure 5 represents the gas chromatogram of TLC fraction obtained on the capillary column (40m).

A typical picture of homologous series of n-paraffins was obtained. Only the peak immediately before n-C_{17} and the peak immediately after n-C_{18} remained unidentified. Complete separation of n-C_{28} and squalene was accomplished by the use of capillary column.

DISCUSSION

Hydrocarbon fraction of vegetable oils was found to contain n-paraffins, isoprenoidal polyolefins, squalene, tri- and tetracyclic diterpenes and compounds with oxygen. Iso-, anteiso- and other branched acyclic hydrocarbons were not identified in any of investigated oil, and it is possible that they are represented by very small peaks which were not analysed.

Oxygen compounds identified were aliphatic and alicyclic ketones, conjugated steroid ketones, esters and lactones. These weakly polar compounds, separated by thin layer chromatography, were found in hydrocarbon fraction. Ethyl ester of fatty acids, found in rapeseed and sunflower oils, are probably the products of transesterification which took place during the saponification of glycerides (22). Alkylacetones, of which hexahydrofarnesylacetone was

found in all investigated oils, had been already mentioned as component of butter, etheric oils of lemon and orange and the fat of Virola Surinamensis (1), but up to now they were not identified in vegetable oils. $\Delta^{3,5}$-steroid-7-ketones which were identified in rapeseed oil showed that this kind of compound could be present in hydrocarbon fraction as well. Lactones, mentioned in rapeseed and sunflower oils, strongly suggest that the appearance of this class of compounds among the hydrocarbons must also be taken into consideration.

Besides n-paraffins, the most abundant hydrocarbons are isoprenoidal polyolefins. Hydrogenation of isomers of molecular weight 408 has shown that binding of carbon atoms in this group of compounds could be accomplished in many ways differeing from the binding in squalene.

The composition of hydrocarbon fractions of investigated oils showed differences which could be used for their characterization: hydrocarbon fraction of rapeseed oil is characterized by the high content of hexahydrofarnesylacetone, n-paraffins, by the presence of two diterpenes (peak 10 and 12), a ketone of formula 2,6,10,14,18,22-hexamethyltricosanone-12 (peak 29) and a compound of formula $C_{29}H_{50}O_2$ (peak 30). This oil does not contain squalene, which is opposite to previous findings (10). Hydrocarbon fraction of sunflower oil is characterized by the high content of hexahydrofarnesylacetone and kaurene (peaks 5 and 9) as well as by n-C_{27}, n-C_{31} and squalene. In olive and pumpkin seed oils, squalene comprises more than 90% of the hydrocarbon fraction. The rest are mainly isoprenoidal polyolefins and n-paraffins. Their gas chromatograms are very similar. The essential difference is that pumpkin seed oil contains a considerable quantity of hexahydrofarnesylacetone and kaurene, whereas olive oil does not contain kaurene. Hydrocarbon fraction of soybean oil practically consists of a homolog series of n-paraffins and squalene. A small quantity of hexahydrofarnesylacetone also was found in soybean oil.

ACKNOWLEDGMENTS

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