Εἰς τὸ τέλος ἑκάστου κεφαλαίου παρατίθεται ἡ βιβλιογραφία. Νομίζω, ὅτι θὰ ἦτο προτιμότερον εἰς τὸ τέλος τοῦ βιβλίου νὰ ὑπάρχῃ εἷς πίναξ βιβλιογραφίας ἀφορῶν εἰς ὅλον τὸ βιβλίον. Ἐπίσης δέον εἰς ἑκάστην βιβλιογραφίαν νὰ ἀναφέρεται ὄχι μόνον ὁ τίτλος τοῦ βιβλίου, ἀλλὰ καὶ ἡ σελίς. Τοιουτοτρόπως διευκολύνεται ὁ ἀναγνώστης, ἐὰν θέλῃ νὰ ἀνατρέξῃ εἰς τὰς πηγάς.

Ἡ παρατήρησις αὕτη δὲν μειώνει τὴν ἀξίαν τοῦ βιβλίου. Ὁ συγγραφεὺς εἶναι ἄξιος ἐπαίνου, διότι, ἀντὶ μετὰ τὰς σπουδάς του νὰ τραπῇ εἰς ἐπαγγελματικὰς ἀσχολίας, ἐτράπη μὲ ἐνθουσιασμὸν πρὸς τὴν ἐπιστημονικὴν ἔρευναν καὶ ἐχάρισε εἰς τὴν Ἑλληνικὴν Ἐπιστήμην ἓν ἄξιον λόγου ἔργον.

ΑΝΑΚΟΙΝΩΣΙΣ ΜΗ ΜΕΛΩΝ

ΧΗΜΕΙΑ ΤΡΟΦΙΜΩΝ.—**Application of short wave ultraviolet spectrophotometry to the analysis of olive oils,** *by Lys. N. Ninnis and M. L. Ninni**. Ἀνεκοινώθη ὑπὸ τοῦ Ἀκαδημαϊκοῦ κ. Ἐμμ. Ἐμμανουήλ.

The high price of olive oil is the main reason why oil is adulterated by mixing it with cheaper vegetable oils.

The conventional examination of the olive oil has been based on specific color reactions and on the determination of its chemical constants. The detection of the vegetable oils by the aformentioned methods was always difficult due to the fact that chemical constants of the adulterated oils are very close in the most cases to the upper limits of pure olive oil. The whole problem became more complicated when the treatment of the vegetable oils by special methods (e.g. decoloration of cotton seed oil by alumina, processing by oxidative compounds) changed the chemical constants and destroyed their specific color reactions.

The ultraviolet spectrophotometry in the region 230-280mμ, fills up the chemical analysis and the existence of a refined oil in a sample of olive oil can

---

* ΛΥΣ. Ν. ΝΙΝΝΗ καὶ ΜΑΡΙΑΣ Λ. ΝΙΝΝΗ, Ἡ χρησιμοποίησις ὑπεριώδους φασματοφωτομετρίας βραχέων κυμάτων εἰς τὴν ἀνάλυσιν τῶν ἐλαιολάδων.

be detected. The detection is based on the observation of J. Guillot (9) that the refined oils possess higher absorption in the ultraviolet than the virgin olive oils. According to G. and W. Wolff (25, 26) the absorptivity at 270mμ for the virgin olive oil is always less than 0,150 and for the refined oils is more than 0,860. Moreover the ratio $R = A_{233}/A_{270}$ in the virgin olive oils is more than 10 and in the refined oils less than 4.

Ultraviolet spectrophotometric work on authentic samples of Greek olive oils has showed that the limits of the absorptivity in this region vary between wide limits and that these limits change from crop to crop (18, 19, 20).

Italian and French workers studying Italian and Tunesian olive oil samples proved that the high absorptivity of the virgin olive oils is generally accompanied by high acidity and then suggested the classification of the virgin olive oils in qualities that could be established according to their absorptivity at 270mμ in combination with the content of free fatty acids. This classification insures the purity of the virgin olive oils (2, 5, 6, 8, 12, 13, 15, 16, 17, 24, 26).

Another method to detect the presence of refined oils in mixtures with virgin olive oils is the objective determination of the small maximum at 270mμ which is developed during the refining of the oils. This is attained by using the constant

$$\Delta K = 1000\ [A_{268} - (A_{262} + A_{274})/2].$$

Virgin olive oils of fine quality have ΔK between —2 and 5 and for the other qualities ΔK is less than 10. The refined vegetable oils have ΔK that varies between 50 and 100 (8,15, 21).

The oxidative deterioration of the natural olive oils increases the absorptivity at 270mμ. The distinction of these oils from the adulterated virgin olive oils is attained by treating them with activated alumina (Al_2O_3). This treatment eliminates the polar products of oxidation which causes the high absorptivity in this region of the spectrum. Under the same conditions the high absorptivity of the refined oils remained unchanged. Absorptivity at 270mμ of previously treated virgin olive oils with alumina more than 0,09 indicate adulterated oils (7, 11, 14).

The methods of ultraviolet spectrophotometry have up to now been limited to the control of the virgin olive oils. The addition of vegetable oils to the refined olive oil cannot be detected by this method. The analysis of the refined olive oil is based on the quantitative determination of its polyunsaturated acids either by spectrophotometry or by gas liquid chromatography (1, 2, 4, 5, 10, 20, 21). Thus an adulterated refined olive oil contains linoleic acid more than 11,0 % and linolenic acid more than 1,0 %.

The aim of this paper was the development of a simple ultraviolet method suitable to control the purity of the virgin and refined olive oil. This is accomplished by working in the short wave ultraviolet region where the absorptivity due to the single double bonds can be used as a degree of the whole unsaturation of the oils (3, 22, 23).

The statistical part of this paper has been based on authentic samples of virgin olive oil gathered by chemists of the Greek Ministry of Commerce from the many oil producing plants of the country.

The samples of pure refined olive oils and their mixtures with virgin olive oil (50:50%) were products of the Elais manufacturing company.

EXPERIMENTAL

A p p a r a t u s. A Unicam S. P. 500 spectrophotometer equipped with stopered silica cells of 10 m.m. optical path was used.

M a t e r i a l s. Cyclohexane showing transmittance more than 10% in the 10 m.m. optical path at 192mμ was used.

P r o c e d u r e. The original solutions for spectrophotometry were made by weighing 0,0700 – 0,0800 gr. of filtered oil and diluting to 25,0 ml with cyclohexane. The absorbance readings were taken by dilution of the original solutions, so that the observed absorbance was between 0,100 and 0,500. The absorptivity has been calculated by using the formula $A = a/bc$, where a is the absorbance, b is the optical path in cm., and c the concentration in gr./100ml.

R e s u l t s. The ultraviolet spectra of some samples of olive and vegetable oils are summarized on a semilog plot in fig. 1.

The statistical results of the absorptivity at the selected wave lenght, the acidity expressed in oleic acid per cent, the index of refraction and the constants ΔK and R of the examined samples of virgin olive oils, refined olive oils and their mixtures have been included in the tables I-IV.

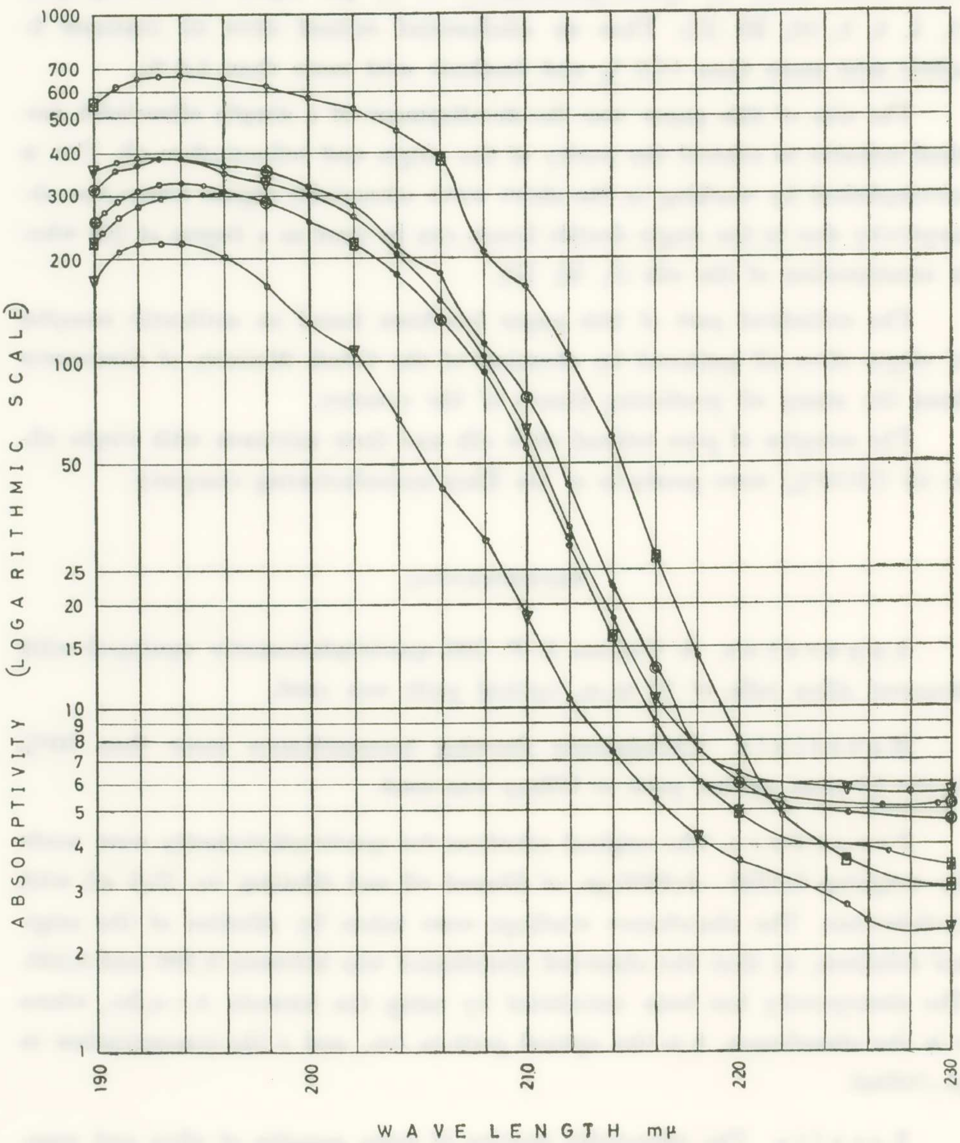

Fig. 1.—Short wave ultraviolet spectra. 1) Olive oil ▼ 2) Sunflower oil ■ 3) Cotton-seed oil ● 4) Soya bean oil ⊙ 5) Corn oil ▽ 6) Linseed oil [·]

TABLE I

Olive oils (crop 1962-1963)

Sample	A_{204}(*)	A_{210}	A_{212}	A_{233}	A_{270}	R	F.F.A.(**)	Refraction(***)
1) Rethymne	64,92	14,29	11,19	2,71	0,633	4,4	4,00	1,4620
2) Cephalonia	66,15	14,32	10,28	2,14	0,336	6,3	9,41	1,4619
3) Kavala	71,23	14,36	12,95	1,61	0,422	3,8	7,00	1,4616
4) Evros	66,82	14,82	13,15	1,87	0,205	9,3	1,30	1,4616
5) Canea	56,86	14,83	10,41	2,96	0,107	6,5	2,82	1,4615
6) Aetolia	65,98	15,24	11,02	1,95	0,220	8,8	4,60	1,4610
7) Boetia	64,34	15,34	11,14	2,50	0,225	11,3	1,76	1,4615
8) Phokis	68,61	15,62	11,59	2,25	0,425	5,3	8,35	1,4614
9) Achaia	64,33	15,78	10,30	2,53	0,410	6,2	2,40	1,4610
10) Chalcidici	64,31	15,78	10,88	3,58	0,278	12,4	7,71	1,4612
11) Kavala	62,17	15,80	10,68	1,58	0,425	3,7	7,01	1,4620
12) Arta	64,36	15,92	10,88	3,58	0,278	12,8	2,59	1,4618
13) Attica	65,43	16,26	10,30	2,53	0,410	6,1	7,11	1,4618
14) Messinia	68,44	16,36	11,16	2,16	0,233	9,8	2,62	1,4617
15) Corinth	68,17	16,66	12,72	3,10	0,272	11,4	4,87	1,4614
16) Zante	62,83	17,01	11,12	4,57	0,394	11,7	1,58	1,4619
17) Arcadia	64,15	17,38	10,70	2,94	0,452	6,5	2,85	1,4615
18) Laconia	65,83	17,50	10,23	1,98	0,250	7,5	3,78	1,4618
19) Messinia	73,97	17,57	11,90	2,07	0,371	5,5	3,32	1,4612
20) Messinia	75,86	17,80	10,83	2,00	0,466	4,3	4,00	1,4620
21) Arta	71,21	17,85	12,53	2,45	0,410	5,9	5,40	1,4615
22) Corfu	67,47	18,32	10,98	2,94	0,342	8,6	5,92	1,4612
23) Phtiotis	64,75	18,61	11,18	3,52	0,520	6,7	6,21	1,4614
24) Heraclion	70,24	19,22	12,09	2,33	0,564	4,2	8,09	1,4612
25) Elias	62,28	19,24	10,35	2,28	0,260	8,7	3,30	1,4612
26) Argolis	79,81	20,16	13,40	2,36	0,409	8,2	5,10	1,4620
27) Dodecanese	78,54	20,52	13,10	1,98	0,240	8,2	6,48	1,4618
28) Magnesia	72,91	20,61	12,05	3,24	0,490	6,5	8,76	1,4620
29) Euboea	79,32	21,16	13,20	2,53	0,600	4,2	9,02	1,4615
30) Samos	75,79	21,52	13,19	3,33	0,416	8,1	6,92	1,4618
Maximum	79,81	21,52	13,40	4,57	0,633	12,8	9,41	1,4620
Minimum	56,86	14,29	10,23	1,61	0,107	3,7	1,30	1,4610

(*) Absorptivity at 204 mμ.

(**) Free fatty acids expressed in oleic acid %

(***) Refractive index at 40°C

TABLE II

Olive oils (crop 1963-1964)

Sample	A_{192}	A_{204}	A_{210}	A_{212}	A_{233}	A_{270}	R	K	F.F.A.	Refraction
1) Cephalonia	238	54,68	13,90	9,20	1,65	0,191	8,6	–8	1,35	1,4615
2) Chalcidici	235	62,70	13,98	9,58	1,76	0,132	13,6	0	1,28	1,4615
3) Rethymne	226	65,23	13,98	9,78	1,86	0,194	9,7	11	5,64	1,4618
4) Canea	233	53,84	14,32	9,46	1,57	0,148	10,4	0	2,48	1,4615
5) Olympia	240	53,87	14,91	9,89	2,19	0,205	10,9	8	1,12	1,4615
6) Achaia	247	62,30	15,10	9,50	1,59	0,166	9,3	6	1,12	1,4612
7) Zante	230	64,61	15,15	10,26	1,74	0,197	8,7	3	1,13	1,4612
8) Aetolia	237	59,05	15,20	10,14	1,81	0,110	16,4	–1	6,40	1,4620
9) Lasithi	245	72,93	15,27	10,10	2,15	0,152	14,3	0	1,91	1,4612
10) Phocis	232	65,72	15,54	10,16	1,80	0,165	11,2	0	3,46	1,4618
11) Laconia	234	71,12	15,60	12,81	1,94	0,236	8,4	13	2,52	1,4615
12) Heraclion	231	63,00	15,66	10,72	2,29	0,259	8,7	0	2,34	1,4615
13) Arcadia	225	61,95	15,70	10,44	1,56	0,169	9,1	4	2,53	1,4615
14) Messinia	238	78,17	15,99	11,23	1,71	0,163	10,6	0	1,24	1,4618
15) Lefcas	228	63,41	16,78	10,82	2,01	0,221	9,1	0	2,74	1,4617
16) Corfu	230	73,75	17,20	11,15	2,14	0,198	10,7	7	2,57	1,4618
17) Preveza	231	70,81	17,53	10,82	2,80	0,238	11,6	–14	4,54	1,4622
18) Lesvos	229	65,99	17,71	10,69	2,29	0,162	14,3	–6	1,52	1,4620
19) Rodopi	239	68,80	18,11	11,59	1,59	0,188	8,3	0	2,14	1,4620
20) Evros	234	73,92	18,23	12,07	2,33	0,267	8,9	7	5,00	1,4621
21) Thesprotea	250	76,10	18,36	11,73	1,79	0,125	14,9	0	3,12	1,4620
22) Euboea	242	65,42	19,12	11,67	2,27	0,262	8,7	14	8,68	1,4615
23) Lesvos	238	73,09	19,80	12,19	2,39	0,182	13,2	2	1,54	1,4620
24) Rhodos	237	81,89	20,04	12,46	2,11	0,160	13,1	7	2,58	1,4620
25) Cyclades	231	53,18	20,10	12,27	1,86	0,238	7,7	0	4,21	1,4620
26) Phtiotis	236	68,25	20,20	13,20	2,63	0,298	8,7	0	5,64	1,4615
27) Kavala	241	80,41	20,46	12,78	2,33	0,204	11,6	0	3,79	1,4623
28) Cos	255	85,10	20,46	12,72	2,25	0,540	4,1	30	4,45	1,4620
29) Arta	238	72,04	20,90	14,05	1,80	0,216	8,5	0	3,73	1,4615
30) Lesvos	240	77,85	21,36	13,40	2,14	0,190	11,2	8	5,61	1,4622
31) Argolis	254	83,82	21,50	13,82	2,91	0,335	8,8	7	3,52	1,4625
32) Attica	252	90,12	21,54	12,72	2,55	0,190	13,4	8	4,65	1,4620
33) Boetia	239	84,32	21,59	14,11	2,20	0,192	11,5	7	1,69	1,4620
34) Corinth	242	71,63	21,60	12,57	3,50	0,643	5,4	9	4,51	1,4622
35) Sciathos	235	69,94	21,62	14,43	2,50	0,273	9,2	0	3,49	1,4622
Maximum	255	90,12	21,62	14,43	3,50	0,643	16,4	30	8,68	1,4625
Minimum	225	53,18	13,90	9,20	1,56	0,110	5,4	–14	1,12	1,4615

TABLE III

Refined olive oils.

No	A_{192}	A_{204}	A_{210}	A_{212}	A_{233}	A_{270}	R	K	Refraction
1	232	71,81	16,30	12,03	2,25	0,683	3,3	62	1,4620
2	231	71,95	16,81	10,86	2,52	0,867	2,9	92	1,4622
3	257	58,82	16,86	11,35	2,33	0,607	3,8	56	1,4619
4	242	76,90	16,96	11,67	2,28	0,600	3,8	60	1,4621
5	220	69,08	16,99	10,27	1,98	0,736	2,6	99	1,4620
6	219	64,22	17,36	10,16	2,08	0,638	3,2	69	1,4621
7	225	69,48	17,54	10,90	2,19	0,614	3,6	73	1,4620
8	263	75,18	17,59	12,13	2,19	0,621	3,5	67	1,4618
9	238	80,51	17,91	11,10	2,22	0,794	2,8	76	1,4619
10	230	76,85	18,22	12,00	2,33	0,816	2,8	73	1,4622
11	248	73,59	18,38	12,09	2,42	0,632	3,8	88	1,4621
12	231	77,61	18,54	11,82	2,44	0,739	3,3	103	1,4622
13	233	73,91	18,54	11,01	1,99	0,760	2,7	103	4,1621
14	240	72,12	21,37	11,83	2,51	0,769	3,3	74	1,4618
Maximum	263	80,51	21,37	12,13	2,52	0,867	3,8	103	1,4627
Minimum	219	58,82	16,30	10,16	1,98	0,600	2,6	56	1,4617

TABLE IV

Mixtures of virgin and refined olive oil (50:50%)

No	A_{204}	A_{210}	A_{212}	A_{233}	A_{270}	R	K	Refraction
1	59,49	14,30	10,91	3,39	0,783	4,8	93	1,4622
2	57,45	15,52	13,50	2,87	0,729	2,5	78	1,4619
3	53,92	15,71	10,50	2,78	0,785	3,5	71	1,4620
4	60,84	16,19	11,06	2,43	0,679	3,5	82	1,4621
5	60,43	16,51	11,29	2,85	0,764	3,8	105	1,4618
6	59,23	18,07	11,95	2,84	0,618	4,5	54	1,4621

DISCUSSION

The short wave ultraviolet absorption spectrum of the olive oil and of some vegetable oils (fig. I) shows clearly, that in the vicinity of 210mμ the greatest differences in absorptivity between olive oil and the vegetable oils were recorded. This fact can be used to insure the purity of the olive oils by measuring the absorptivity at 210mμ.

Statistical work on genuine pure samples of Greek olive oils, of the crops 1962-1963 and 1963-1964 proved, that the absorptivity varies between 13,8 and 21,6 at 210mμ (tables I and II). The absorptivity of the examined samples of sunflower oils, corn oils, cottonseed oils and soya bean oils varies between 56,0 and 78,5 (fig. 1). The above results show clearly, that the detection of the vegetable oils in mixtures with olive oils is always possible if the amount of added oil is more than 20%, while in the most cases as low as 5% is detectable.

The proposed method is not restricted to control only the purity of the fine quality virgin olive oil, but can be used, as a general method, in the analysis of all kinds of olive oil, e.g. refined olive oil, high acidity olive oil, mixtures of virgin and refined olive oil (tables I, II, III, IV).

The combination of the absorptivities at 210mμ and 270mμ with the constants ΔK and R is useful in obtaining more documents relating to the quality of the examined olive oil. Thus by using the aforsaid ultraviolet data it is possible to distinguish the following cases.

1) *Fine quality pure virgin olive oil.* Absorptivity at 210mμ less than 21,5 at 270mμ less than 0,250, ΔK less than 5 and R more than 10.

2) *Pure olive oil in early stages of oxidative attack.* Absorptivity at 210mμ less than 21,5, at 270mμ more than 0,250, ΔK more than 5 and R less than 10.

3) *Adulterated virgin olive oil.* Absorptivity at 210mμ more than 21,5, at 270mμ more than 0,250, ΔK more than 10 and R less than 10.

4) *Pure refined olive oil.* Absorptivity at 210mμ less than 21,5, at 270mμ more than 0,500, ΔK more than 50 and R less than 4.

5) *Adulterated refined olive oil.* Absorptivity at 210mμ more than 21,5, at 270mμ more than 0,500, ΔK more than 50 and R less than 4.

Acknowledgment. Special thanks are due to the Ministry of Commerce, General Technical Directorate and to the ELAIS Manufacturing Company, for the supply of the samples of original olive oil.

ΠΕΡΙΛΗΨΙΣ

Στατιστικὴ ἔρευνα διεξαχθεῖσα ἐπὶ αὐθεντικῶν δειγμάτων παρθένου ἐλαιολάδου, παραγωγῆς 1962 - 63 καὶ 1963 - 64, εἰς τὴν περιοχὴν τῶν βραχέων κυμάτων τοῦ ὑπεριώδους φάσματος ἀπέδειξεν, ὅτι ἡ περιοχὴ τῶν 210 mμ εἶναι ἡ

πλέον κατάλληλος διὰ τὴν ἀνίχνευσιν τῶν διὰ σπορελαίων νοθεύσεων τοῦ ἐλαιολάδου. Οὕτω ἡ εἰδικὴ ἀπορρόφησις τοῦ ἐλαιολάδου εἰς 210 mμ κυμαίνεται μεταξὺ 13,8 - 21,6, ἐνῷ τῶν συνήθων σπορελαίων κυμαίνεται μεταξὺ 56,0 - 78,5.

Ἡ ὡς ἄνω μέθοδος δὲν περιορίζεται, ὅπως αἱ χρησιμοποιούμεναι μέχρι σήμερον μέθοδοι ὑπεριώδους φασματοφωτομετρίας, εἰς τὸν ἔλεγχον τῆς καθαρότητος τοῦ καλῆς ποιότητος ἐλαιολάδου, ἀλλὰ δύναται νὰ χρησιμοποιηθῇ ὡς γενικὴ μέθοδος εἰς τὴν ἀνάλυσιν ὅλων τῶν εἰδῶν ἐλαιολάδου, ἤτοι παρθένου, παλαιοῦ μεγάλης ὀξύτητος, ἐξηυγενισμένου καὶ τῶν μειγμάτων παρθένου καὶ ἐξηυγενισμένου.

REFERENCES

1. Albonico, F., and M. Vitagliano, Olearia, **12**,5 (1959).
2. Albonico, F., and A. Vodret, Olearia, **14**,57 (1960).
3. Barnes, R., J. Rusoff, E. Miller and G. Burr, Ind. Eng. Chem. (Anal. Ed.). **16**, 385 (1947).
4. Caroglio, P., and G. Giannardi, Olearia, **15**, 189 (1961).
5. Doro, B., and V. Sadini, Boll. Lab. Chim. Provinciali, **10**, 124 (1959).
6. Doro, B., V. Sadini and G. Gabucci, Boll. Lab. Chim. Provinciali, **11**, 499 (1960).
7. Doro, B., and S. Remoli, Boll. Lab. Chim. Provinciali, **13**, 488 (1962).
8. Fabris, A., and M. Vitagliano, Olii Minerali Grassi e Saponi Colori e Vernici, **36**, 313 (1959).
9. Guillot, J., Ann. Fals. Fraudes, **28**, 69 (1935).
10. Kaufmann, H., and M. Aparicio, Annales Inst. Invest. Vet. (Madrid) **11**, 179 (1961).
11. Laporta, L., and M. Jacone, Rev. Ital. Sost. Grasse, **38**, 131 (1961).
12. Mattei, R., and G. Volpi, Olearia, **13**, 55 (1959).
13. Montefredine, A., and L. Laporta, Olii Minerali Grassi e Saponi Colori e Vernici, **36**, 31 (1959) and **36**, 325 (1959).
14. Montefredine, A., and L. Laporta, Boll. Lab. Chim. Privinciali **13**, 498 (1962).
15. Morani, V., and C. Marignoli-Colloca, Olii Minerali Grassi e Saponi Colori e Vernici **8**, 327 (1959).
16. Minutilli, F., and G. Ruggieri, Rass. Chim. **13**, 8 (1961).
17. Minutilli, F., Rass. Chim., **13**, 14 (1961).
18. Ministry of Commerce, Kingdome of Greece, Study of the Greek Olive Oil, Crop. 1962-1963.
19. Ninnis, L. N., and M. L. Ninni, Prakt. Acad. Athenon, **31**, 97 (1956).
20. Ninnis, L. N., and M. L. Ninni, Prakt. Acad. Athenon, **33**, 103 (1958).
21. Ruggieri, G., and F. Minutilli, Rass. Chim., **13**, 19 (1961).
22. Rusoff, J., J. Platt, H. Klevens and G. Burr, J. Am. Chem. Soc., **67**, 673 (1945).
23. Schauenstein, E., and G. Benedict, Fette-Seifen und Anstrichmitteln, **62**, 687 (1960).
24. Uzzan, A., Olii Minerali Grassi e Saponi Colori e Vernici, **8**, 307 (1959).
25. Wolff, G., and J. Wolff, ITERG, **6**, 379 (1952).
26. Wolff, J., Rev. Franc. Corps Grass, **1**, 215 (1954) and **3**, 17 (1956).