193. The Chemistry of Ximenynic Acid.

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The isolation of ximenynic acid from the kernel oils of three *Ximenia* species is described. Degradative experiments show the acid to be heptadec-10-en-8-yne-1-carboxylic acid, but attempts to produce isomerisation about the double bond and to reduce the acid to the corresponding conjugated dienoic acid were unsuccessful. When heated with alkali at 180—190°, ximenynic acid isomerises to a conjugated trienoic acid.

The behaviour of ximenynic acid and its methyl ester towards the Wijs, Woburn, and Rosenmund–Kuhnhenn reagents has been studied. Ximenynic acid and its derivatives autoxidise readily, but the glycerol, pentaerythritol, and inositol esters are not suitable for use as drying oils.

IN a preliminary communication (Ligthelm and Schwartz, *J. Amer. Chem. Soc.*, 1950, **72**, 1868), the isolation of an acid, $C_{18}H_{30}O_2$, from the kernel oils of three South African *Ximenia* species was described. The acid was named ximenynic acid, and it was shown to be a C_{18}

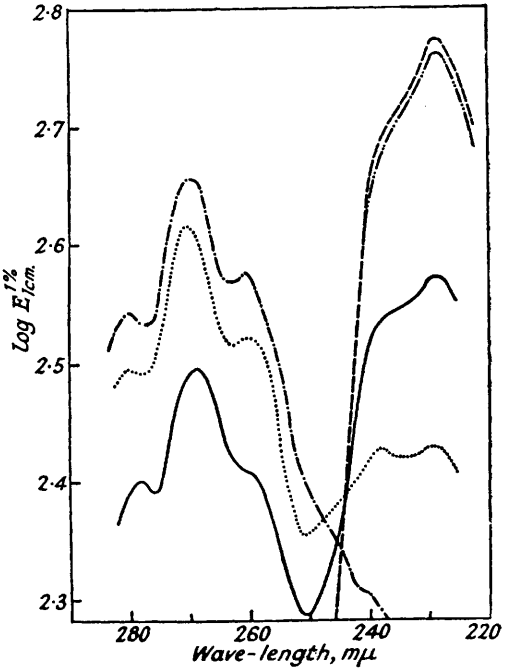
straight-chain acid containing one double and one triple bond. From the products of its oxidation with potassium permanganate and from the absorption spectrum of ximenynyl alcohol (Ligthelm, von Rudloff, and Sutton, *J.*, 1950, 3187), it was clear that the acid is either (I) or (II). We now report a further examination of the acid, that of the oils being

(I) $CH_3\cdot[CH_2]_5\cdot CH{:}CH\cdot C{\vdots}C\cdot[CH_2]_7\cdot CO_2H$ $CH_3\cdot[CH_2]_5\cdot C{\vdots}C\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$ (II)

recorded elsewhere (*J. Sci. Food Agric.*, in the press).

Ximenynic acid is best isolated from the mixed acids of *Ximenia* oils by a combination of low-temperature crystallisation and high-vacuum distillation, an improvement in the former process being described on p. 1090. Ximenynic acid of 90—95% purity can also be obtained in good yield by chromatography of the acids or methyl esters on silica gel (Riemenschneider, Herb, and Nichols, *J. Amer. Oil Chem. Soc.*, 1949, **26**, 371) or alumina (Swift, Rose, and Jamieson, *Oil and Soap*, 1943, **20**, 249), especially when the starting mixtures contain more than 50% of the acid or ester. Preliminary concentration of ximenynic acid may be effected by formation of the urea complex from the total acids or the methyl esters (Schlenk and Holman, *J. Amer. Chem. Soc.*, 1950, **72**, 5001); *e.g.*, a single fractionation by this method of the total methyl esters of *Ximenia caffra* oil raised the methyl ximenynate content from 27 to 50% in the raffinate, but further concentration was not attained by refractionation. The urea complexes of the acid, methyl ester, and alcohol have been prepared, and their properties recorded. The "yield value" (Schlenk and Holman, *loc. cit.*) of the ester is lower than that of the acid and hence the former was used in the above purification experiments.

The ultra-violet absorption spectrum of the purest specimen of ximenynic acid obtained is shown in the figure, together with that of ximenynyl alcohol. Both compounds exhibit the main peak (at 229 mμ) characteristic of conjugated enynes; the inflections of low intensities near 268 mμ are attributed to the presence of a trace (*ca.* 0·1%) of conjugated triene acid which accompanies the ximenynic acid during purification.



— · · — *Ximenynic acid.*
— — — *Ximenynyl alcohol.*

Ximenynic acid after isomerisation by alkali for : 25 *min.* ——; 60 *min.* – – – –; 120 *min.* — · — · —.

Ozonolysis of ximenynic acid followed by decomposition of the ozonide with zinc and acetic acid (Noller and Adams, *J. Amer. Chem. Soc.*, 1926, **48**, 1074) gave *n*-heptanaldehyde and azelaic acid in quantity, and a trace of what was possibly azelaic semialdehyde derived from the conjugated triene impurity. It follows that ximenynic acid is heptadec-10-en-8-yne-1-carboxylic acid (I). Attempts to confirm this structure by synthesis and to determine whether the ethylenic bond has the *cis*- or the *trans*-configuration are in progress. Since most natural fatty acids have the *cis*-configuration, attempts were made to effect a *cis*–*trans*-change in ximenynic acid by heating it with selenium (Swern, Knight, Shreve, and Heether, *J. Amer. Oil. Chem. Soc.*, 1950, **27**, 17), but only unchanged acid was obtained.

When the acid or its methyl ester is heated with potassium hydroxide in ethylene glycol at 180—190° the maximum at 229 mμ is replaced by maxima at 260, 268, and 280 mμ characteristic of conjugated trienoic acids. The intensity of the central (268 mμ) absorption band reaches a maximum after 120 minutes at 180° or 60 minutes at 190° (see figure); longer heating causes diminution in the intensity, presumably owing to subsequent polymerisation of the triene system. No change in the absorption spectrum of ximenynic acid, except a slight lowering of intensity, occurs when it is heated in ethylene glycol in the absence of alkali. Lithium aluminium hydride reduction of the crude isomerised acids gives a product with the same three absorption bands but of slightly greater intensity, indicating that no conjugation exists between the carbonyl group and the chromophoric system. A small yield of a crystalline acid, m. p. 60—61°, $E^{1\%}_{1\,\text{cm.}}$ 1705 at $\lambda_{\text{max.}}$ 268 mμ, was obtained by recrystallisation of the crude alkali-isomerised product. The products of permanganate oxidation of this acid appeared to contain mixtures of mono- and di-carboxylic acids, suggesting that isomeric heptadecatriene-1-carboxylic acids were present in the material of m. p. 60—61°; attempts to identify the oxidation products are being made. The isomerisation with alkali of the enyne system to a conjugated triene is of interest since Maruyama and Suziki (*Proc. Imp. Acad. Tokyo*, 1931, **7**, 265) reported the the conversion of heptadeca-7 : 9-diene-1-carboxylic acid into stearolic acid under similar conditions.

Attempts to convert the enyne system of ximenynic acid into the corresponding conjugated diene by partial hydrogenation by using a quinoline-poisoned palladium catalyst (Isler, Huber, Ronco, and Kofler, *Helv. Chim. Acta*, 1947, **30**, 1911) were unsuccessful; the products had less intense absorption in the 229—234 mμ region, whereas heptadeca-8 : 10-diene-1-carboxylic acid has $E^{1\%}_{1\,\text{cm.}}$ 1100 at $\lambda_{\text{max.}}$ 232 mμ. Attempted reduction with sodium and alcohol gave a product with lower intensity at 229—234 mμ. However, catalytic hydrogenation of ximenynyl alcohol by means of the quinoline-poisoned catalyst gave an increased ultra-violet absorption ($E^{1\%}_{1\,\text{cm.}}$ 670 at 229 mμ), indicating the formation of some of the desired conjugated diene system, but the experiments were too unpromising for further study.

It is well known that many acetylenic compounds add one mol. of halogen readily, but the second mol. with difficulty (Johnson, "The Chemistry of the Acetylenic Compounds," Arnold, London, Vol. 2, p. 57, 1950). In conformity, ximenynic acid gave low iodine values (absorption of *ca.* 1·5 moles of halogen per mole) with the Woburn (von Mikusch and Frazier, *Ind. Eng. Chem. Anal.*, 1941, **13**, 782) and the Wijs method ("Official and Tentative Methods of the American Oil Chemists' Society," Chicago, 1946), but values corresponding to *ca.* 2 moles per mole with the modified Rosenmund–Kuhnhenn method (Benham and Klee, *J. Amer. Oil Chem. Soc.*, 1950, **27**, 127, 130). If the reaction time in the Woburn method was increased to 96 hours, an addition of 2 moles per mole was obtained, and addition of bromine vapour to the acid or its methyl ester gave a similar result (private communication from Dr. F. Hawke).

Methyl ximenynate autoxidises rapidly in air and the parent acid does so more slowly. The glycerol, pentaerythritol, and inositol esters were prepared and tested for drying properties on glass plates in the presence of inorganic driers; the speed of setting increased in that order, but all the films remained tacky for at least 48 hours.

EXPERIMENTAL

($E^{1\%}_{1\,\text{cm.}}$ values were measured in *cyclo*hexane, except where otherwise stated.)

Isolation of Ximenynic Acid.—(a) *Preferred method.* In a typical run the mixed fatty acids of *Ximenia caffra* oil (406 g.; $E^{1\%}_{1\,\text{cm.}}$ 148·3 at 229 mμ) were crystallised from acetone (10 ml. per g.) at −25°. The soluble fraction (226 g.; $E^{1\%}_{1\,\text{cm.}}$ 197 at 229 mμ) in light petroleum (b. p. 40—60°; 5 ml. per g. of acids) was kept at −22° for 5 hours. The insoluble acids (60 g.; $E^{1\%}_{1\,\text{cm.}}$ 447 at 229 mμ; neutralisation equiv., 292) were converted into methyl esters and fractionally distilled under high vacuum; the fractions with saponification equivalent 293—294 and $E^{1\%}_{1\,\text{cm.}} > 450$ at 229 mμ were combined and hydrolysed, and the acids recrystallised from acetone and light petroleum (Ligthelm and Schwartz, *loc. cit.*), to give white plates, m. p. 39—40° (corr.); $E^{1\%}_{1\,\text{cm.}}$ 583 ± 2 at 229 mμ, $E^{1\%}_{1\,\text{cm.}}$ 2·5 at 268 mμ. The overall yield was 4—7% of the total fatty acids, *i.e.*, 15—28% of the ximenynic acid present in the starting material.

(b) *By chromatography* (cf. Swift, Rose, and Jamieson, *loc. cit.*). Alumina (100 g.; Peter Spence, chromatographic grade) was treated with a little water and ethyl acetate and then heated at 145° for 1 hour. The mixed methyl ximenynate concentrates (1·0560 g.; $E^{1\%}_{1\,\mathrm{cm.}}$ 325 at 229 mμ; sap. equiv., 294—295) in light petroleum (10 ml.) were slowly poured on a column of alumina (2 × 30 cm.) and then eluted with solvents as follows : (i) 200 ml. of light petroleum, then (ii) 100 ml., (iii) 60 ml., (iv) 80 ml., (v) 60 ml., (vi) 50 ml. of 5, 10, 10, 10, and 50%, respectively, of ether in light petroleum, (vii) ether, and (viii) benzene–ethanol. The total recovery was 96·2%, most of the material being in eluants (ii)—(iv), and that in eluants (iii) and (iv) having $E^{1\%}_{1\,\mathrm{cm.}}$ at 229 mμ = 527 and 523, respectively. With more active alumina, lower recoveries were obtained, and " active " alumina did not give any separation.

In other experiments silica gel (Davison Chemical Corp., Baltimore, U.S.A., " grade through 200 mesh ") and Hyflo Supercel (Johns Mansville, U.S.A.) in a ratio of 80 : 20 was the adsorbent; this (30 g.) was well mixed and activated at 190—200° for 1 hour, then tightly packed in a column (2·4 × 50 cm.) and wetted with light petroleum (60 ml.). The mixed acids (1·0268 g.; $E^{1\%}_{1\,\mathrm{cm.}}$ 295 at 229 mμ) were dissolved in light petroleum (10 ml.) and poured on the column, which was then eluted by : (i) 200 ml. of 10% benzene in light petroleum; (ii) 200 ml. of 1% ether in light petroleum; then 100 ml. each of (iii) 2·5%, (iv) 5%, (v) 5%, (vi) 5%, (vii) 10%, (viii) 15% ether in light petroleum, and (ix) ether alone. The weights (mg.) and (in parentheses) values of $E^{1\%}_{1\,\mathrm{cm.}}$ at 229 mμ were : (i) 3·8 (—), (ii) 0 (—), (iii) 112·4 (333), (iv) 263·7 (12), (v) 200·2 (358), (vi) 132·4 (540), (vii) 134·7 (506), (viii) 90·7 (549), (ix) 66·5 (350); total recovery, 97%.

(c) *By urea-complex formation.* The methyl esters (10 g.; $E^{1\%}_{1\,\mathrm{cm.}}$ 148 at 229 mμ) of *Ximenia caffra* oil and methanol saturated with urea at room temperature (300 ml.) were heated till homogeneous and then left for 3 hours at 31°. The crystals were collected (fraction A), and the filtrate kept overnight at room temperature (15°) to give a second crop (B) of crystals. The filtrate (C) and fractions (A) and (B) were suspended in separate quantities of water containing a little concentrated hydrochloric acid and the aqueous phases were extracted twice with light petroleum. The petroleum solutions were washed with water, the solvent was evaporated, and the residues were dried. The weights and the $E^{1\%}_{1\,\mathrm{cm.}}$ values at 229 mμ of the different fractions were :

Fraction	Wt., g.	$E^{1\%}_{1\,\mathrm{cm.}}$	% of total ximenynic acid in fraction	Fraction	Wt., g.	$E^{1\%}_{1\,\mathrm{cm.}}$	% of total ximenynic acid in fraction
A	5·6	57·1	21·6	C	0·8	279	15·1
B	2·8	277	52·5	Loss	0·8	—	10·8

Esters.—*Methyl ximenynate* was prepared from the acid (20 g.) and isolated in the usual way (Hilditch, " Chemical Constitution of Natural Fats," 2nd edn., J. Wiley and Sons, New York, 1947, p. 474); yield, 21·0 g. (100%), b. p. 148°/0·2 mm., 163—165°/0·4 mm., 172—174°/0·8 mm., n_{D}^{25} 1·4700, d_{25}^{25} 0·9067, $E^{1\%}_{1\,\mathrm{cm.}}$ 549·2 at 229 mμ (Found : C, 77·5; H, 11·1%; sap. equiv., 292·9. $C_{19}H_{32}O_2$ requires C, 78·0; H, 11·0%; equiv., 292·4). The ester became yellow in the air, and after 30 minutes had absorbed *ca.* 2% of oxygen (Found : C, 76·45; H, 10·7%).

Ethyl ximenynate, similarly prepared (5·4 g. from 5 g. of acid), had b. p. 168—169°/0·2 mm., n_{D}^{25} 1·4680, $E^{1\%}_{1\,\mathrm{cm.}}$ 525 at 229 mμ (Found : C, 78·4; H, 11·2%; sap. equiv., 306·9. $C_{20}H_{34}O_2$ requires C, 78·25; H, 11·25%; equiv., 306·6).

Ximenynamide.—This *amide* formed small yellow nest-like crystals, m. p. 105—105·5° (Found : C, 78·3; H, 11·3. $C_{18}H_{31}ON$ requires C, 77·9; H, 11·3%).

p-*Bromophenacyl Ximenynate.*—The *ester,* recrystallised from alcohol, had m. p. 53·8—54·2° (Found : C, 65·8; H, 7·5. $C_{26}H_{35}O_3Br$ requires C, 65·7; H, 7·4%).

Urea Complexes of Ximenynic Acid and Its Derivatives.—These complexes were prepared essentially as described above, recrystallised from *iso*propyl alcohol, and dried in a vacuum. The $E^{1\%}_{1\,\mathrm{cm.}}$ values at 229 mμ were determined (alcoholic solution), and the molar ratio of urea to compound calculated. The results were as follows :

Complex with :	Yield value	$E^{1\%}_{1\,\mathrm{cm.}}$ at 229 mμ	M. p.	Mols. urea/ mol. compound
Ximenynic acid	1·55	132·0	130·5—131·5°	16·0
Methyl ximenynate	1·0	132·6	133—135	15·2
Ximenynyl alcohol	1·0	150·4	133—135	12·1

Ozonolysis of Ximenynic Acid.—A stream of ozonised oxygen (2·5% of ozone) was passed through a solution of ximenynic acid (3 g.) in glacial acetic acid (20 ml.) for 150 minutes, the solution being kept at 15—20° to reduce loss of acetic acid. To the solution were added zinc dust (6·5 g.) and a trace of water, the whole was refluxed with stirring for 90 minutes, and water was added. The product was filtered off and well washed with ether, the combined filtrate was washed with water and dried ($CaCl_2$), and the ether removed by distillation through a column. The residue was fractionally distilled to give five fractions : (*a*) b. p. 100—120°/650 mm. (*ca.* 3 g.); (*b*) b. p. 120—123°/650 mm. (*ca.* 2 g.); (*c*) b. p. 123°/650 mm.—60°/20 mm. (0·2 g.); (*d*) b. p. 160—167°/0·5 mm. (*ca.* 0·18 g.); (*e*) b. p. 175°/0·5 mm. (*ca.* 0·5 g.). Fraction (*a*) was chiefly acetic acid. Fraction (*b*) contained heptanaldehyde, which formed a semicarbazone (0·3 g.), m. p. 107—109° after one crystallisation from aqueous alcohol (Found : C, 56·3; H, 10·55. Calc. for $C_8H_{17}ON_3$: C, 56·1; H, 10·05%), the m. p. being undepressed when the material was mixed with an authentic sample, m. p. 108—109°. Fraction (*c*) also contained heptanaldehyde (oxime, m. p. and mixed m. p. 54·5°); (*d*) consisted chiefly of azelaic acid, also obtained (0·4 g.) by recrystallisation of (*e*) from ethyl acetate and *iso*heptane; it had m. p. and mixed m. p. 106—107° (Found : C, 57·7; H, 8·9%; equiv., 96·7. Calc. for $C_9H_{16}O_4$: C, 57·4; H, 8·6%; equiv., 94·1). The mother-liquors from the crystallisation of (*e*) were concentrated and boiled with an excess of semicarbazide to give 15 mg. of semicarbazone, m. p. 141—149°, which after four recrystallisations from aqueous alcohol yielded *ca.* 1 mg., m. p. 158—160° (azelaic semialdehyde semicarbazone has m. p. 162°; Scanlan and Swern, *J. Amer. Chem. Soc.*, 1940, **62**, 2305).

Attempted " Elaidinisation " of Ximenynic Acid.—Ximenynic acid (1·4 g.) was treated by the method of Swern *et al.* (*loc. cit.*) (selenium, 0·007 g.; 200°; 2 hours), but the material isolated was unchanged acid (0·48 g.; m. p. and mixed m. p.).

Attempted Reduction of Ximenynic Acid to the Dienoic Acid.—Methyl ximenynate (1·5 g.), reduced by Adams and Marvel's method (*J. Amer. Chem. Soc.*, 1920, **42**, 310), yielded 1·1 g. of product, $E^{1\%}_{1\,\text{cm.}}$ 464 at 229 mμ. Reduction of the acid (41·1 mg.) by use of a poisoned palladium–charcoal catalyst (Isler *et al.*, *loc. cit.*) until one mol. of hydrogen had been absorbed (5 min.) afforded a product with $E^{1\%}_{1\,\text{cm.}}$ 232 at 229 mμ. The hydrogenation was thus largely unselective. Since Dr. Isler stated (private communication) that the presence of any acid will destroy the toxicity of the catalyst, an experiment was conducted on ximenynyl alcohol (0·05 g.), a sample of poisoned catalyst being used which was obtained from Messrs. Hoffman–La Roche, Switzerland; after absorption of 1 mol. of hydrogen (5 min.), the product isolated had $E^{1\%}_{1\,\text{cm.}}$ 670 at 229 mμ, which indicated that the hydrogenation was still largely unselective.

Iodine Values of Ximenynic Acid and Methyl Ximenynate.—The modified methods described above were used, but in preparing the modified Rosenmund–Kuhnhenn reagent, the acetic acid and bromine were cooled before being mixed, because a reaction took place between them at room temperature; the iodine values found with the different reagents are summarised below :

	Acid	Ester
I.V., calc.	273·6	260·6
I.V., calc. for 2 mols. of halogen	182·5	173·8

Woburn method			Wijs method			Rosenmund–Kuhnhenn method		
Hours	Acid	Ester	Hours	Acid	Ester	Hours	Acid	Ester
1	151·9	140·5	1	130·3	124·8	1	193·3	174·9
2	148·1	137·1	2	131·0	125·5	2	196·6	178·9
10	157·4	141·7	10	129·7	124·5			
24	153·7	142·6	24	127·5	120·5	Bromine-vapour method *		
48	161·0	144·2	48	127·5	124·5	1	187·1	170·3
96	189·2	168·7						

* Data obtained from Dr. F. Hawke, Department of Chemistry, University of the Witwatersrand, Johannesburg.

Alkali Isomerisation of Ximenynic Acid.—This process was carried out according to *J. Amer. Oil Chem. Soc.*, 1949, **26**, 399, except that air was excluded. A weighed quantity of the acid or methyl ester (*ca.* 0·1 g.) and ethylene glycol–potassium hydroxide reagent (10 ml.) were placed in a tube, which was then evacuated, sealed, and heated at 180° ± 0·5° for various times. The tubes were cooled under the tap and opened, the contents quantitatively transferred to 100-ml. volumetric flasks, and the volumes made up with purified 96% alcohol. The absorptions were measured in a Beckman spectrophotometer Model DU, after suitable dilution; the results were :

	$E^{1\%}_{1\,\text{cm.}}$ at :				$E^{1\%}_{1\,\text{cm.}}$ at :		
Time, min.	229 mμ	234 mμ	268 mμ	Time, min.	229 mμ	234 mμ	268 mμ
25	367	353	432	60	217	235	590

To obtain the free acids, the contents of each tube were poured into 20 ml. of water, the solutions just acidified with concentrated hydrochloric acid, and the acids extracted with light petroleum. After evaporation of the petroleum the residue was dried in a vacuum at 80—100°. The absorption in the ultra-violet region was examined in *cyclo*hexane solution with the results summarised below :

Temp.	Duration of heating (min.)	$E^{1\%}_{1\,\text{cm.}}$ at 229 mμ	$E^{1\%}_{1\,\text{cm.}}$ at 268 mμ	Temp.	Duration of heating (min.)	$E^{1\,\text{cm.}}_{1\%}$ at 229 mμ	$E^{1\,\text{cm.}}_{1\%}$ at 268 mμ
180°	0	583	2·5	190°	60	155	450
—	25	376	315	—	90	115	425
—	60	251	388	—	120	98	385
—	90	195	420				
—	120	170	455				

The product isomerised at 180° was reduced with lithium aluminium hydride (Ligthelm, von Rudloff, and Sutton, *loc. cit.*). The reduced material was dried, yielding a product with $E^{1\%}_{1\,\text{cm.}}$ 456 at 268 mμ. The isomerised acids were crystallised as follows : The acids from the alkali-isomerisation product were dissolved in light petroleum (10 ml. per g. of acid) and left at 0° for a few hours. A brown oil which separated from the solution was removed, and the solution cooled to —60°, to give a white precipitate which was collected on a cooled Buchner funnel and recrystallised twice from light petroleum at —10°, yielding white crystals, m. p. 60—61°; $E^{1\%}_{1\,\text{cm.}}$ 1705 at $\lambda_{\text{max.}}$ 268 mμ, $E^{1\%}_{1\,\text{cm.}}$ 130 at 229 mμ (no maximum). The acid was soluble in dilute alkali and in most organic solvents; it oxidised very rapidly in air with formation of an oil.

Glycerol, Pentaerythritol, and Inositol Esters of Ximenynic Acid.—These esters were prepared according to Wheeler, Riemenschneider, and Sando's method (*J. Biol. Chem.*, 1940, **132**, 687). A weighed quantity of the alcohol (0·3 g.), a slight excess over 1 equiv. of ximenynic acid, and toluene-*p*-sulphonic acid (0·05 g.) were placed in 12″ × 1″ test-tubes, and the tubes evacuated to 0·05 mm. and heated until evolution of gas ceased. The glycerol, pentaerythritol, and inositol esters formed at 150°, 200—220°, and 250°, respectively. After the reaction was completed, the tubes were cooled, the contents dissolved in light petroleum (b. p. 40—60°) or ether, and the solutions washed with 5% potassium carbonate solution; the solvents were then removed. The residual material was taken up in a small volume of mineral turpentine, a few drops of drier (containing 0·5% Pb, 0·05% Co, and 0·03% Mn) added, and the films spread on glass plates and regularly tested for drying (touched with the finger). The inositol, pentaerythritol, and glycerol esters set after about 10, 15, and 20 hours, respectively. All the films, however, after 48 hours' exposure still had a pronounced "after tack," which was only lost after exposure to direct sunlight. After a few weeks the original solutions separated into two phases.

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