for vinyl resins. Their performance in a series of additional epoxy plasticizers of vegetable and marine origin is described. Novel epoxy plasticizers based upon mixed acetylated mono- and di-glyceride have been prepared and are found to have excellent plasticizer performance.

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Evidence for Cyclic Monomers in Heated Linseed Oil[1]

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THE DISTILLABLE ETHYL ESTERS prepared from heated linseed oil have been shown by Wells and Common (24) to contain a fraction that fails to form an adduct with urea. Part of the deleterious effect of heated linseed oil on the nutrition of the rat (9, 11) is associated with this non-urea-adduct-forming distillable fraction (NAFD) (10).

Wells and Common (24) have suggested that the failure of NAFD to form an adduct with urea may be due to the presence of a non-terminal ring structure. The presence of cyclic monomers among the products of the heat treatment of glycerides and fatty esters has often been suggested (*e.g.*, 5, 21), but until recently the evidence for them has been indirect. Phthalic acid has been detected, by means of color reactions, among the products of the oxidation of heated linseed oil (7). Boelhouwer, Jol, and Waterman (4), employing a graphical-statistical method of ring analysis, showed that the monomeric products obtained from the heat treatment of linseed oil contain ring compounds. Mehta and Sharma (17) concluded that intra-acyl cyclization during the early stages of the heat-bodying of linseed oil is the chief cause of the initial rapid drop in iodine number without corresponding increase in molecular weight.

Recently Paschke and Wheeler (18) obtained direct chemical evidence for the existence of six-membered rings in the monomeric products of the heat treatment of methyl eleostearate. The heat treatment of various esters, and of sunflower seed oil, yields dimeric products which have been shown by Clingman, Rivett, and Sutton (8) to be cyclic. However no such chemical evidence has been obtained for cyclic compounds in the monomeric products from unconjugated esters or glycerides.

In the present investigation evidence for cyclic monomers in the NAFD of heated linseed oil has been obtained by methods involving aromatization *via* allylic bromination and dehydrohalogenation, followed by oxidation to a simple aromatic acid (8, 18).

Experimental[2]

Preparation of NAFD. Alkali-refined and bleached linseed oil was stripped at 170°C. in a centrifugal molecular still[3] and then heated at 275 ± 3°C. for 12 hr. A stream of purified nitrogen sufficient to maintain vigorous agitation was passed through the oil during the heating period. The heated oil had the following characteristics: kinematic viscosity (Fenske viscometer), 306 centistokes at 25°C.; n_D^{20} 1.48533; iodine number (4 hr., Benham and Klee method [14, 15]), 163. It was converted to ethyl esters by alkali-catalyzed ethanolysis, and the esters were distilled in the centrifugal molecular still. Fifty per cent of the

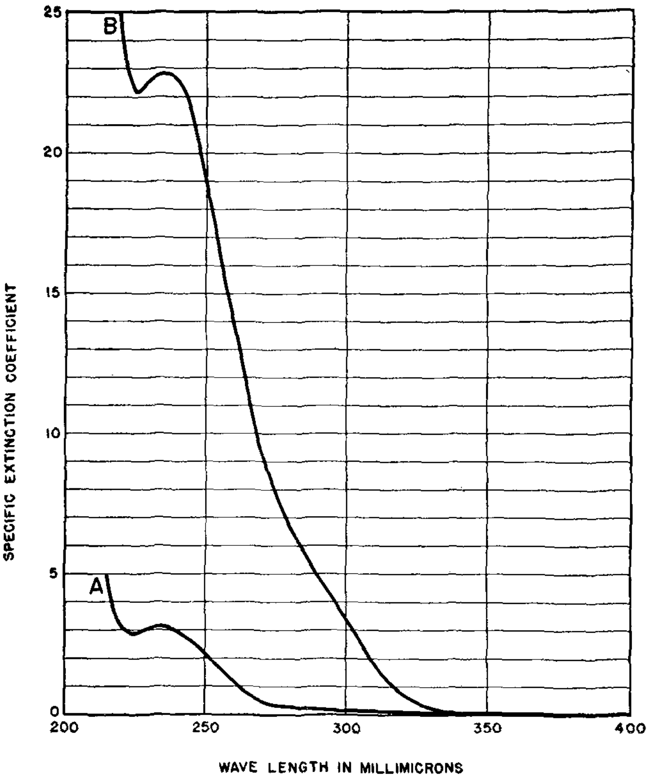

FIG. 1. Ultraviolet spectra of NAFD (Curve A) and aromatized NAFD (Curve B) in isöoctane at concentrations of 0.347 and 0.404 g./l. respectively.

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[1] Issued as N.R.C. No. 4001.

[2] Melting points are uncorrected.

[3] Model No. CMS-5, manufactured by Distillation Products Industries. The pressure in the system was one micron when distillation was not in progress.

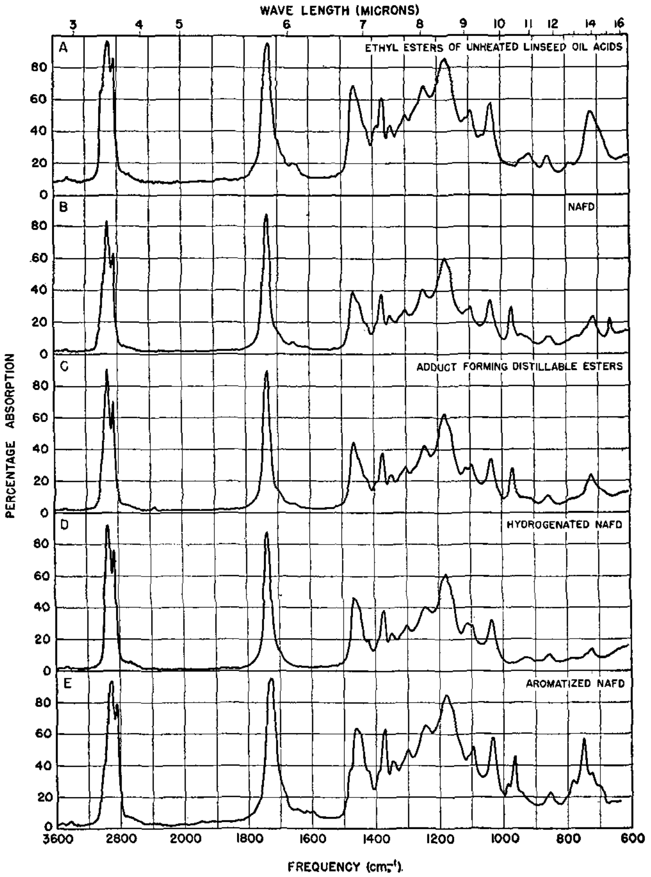

Fig. 2. Infrared spectra. A. Ethyl esters of unheated linseed oil acids. B. NAFD. C. Adduct-forming distillable esters. D. Reduced NAFD. E. Aromatized NAFD. Spectra were run on the undiluted oils.

esters were collected at a temperature of 60°C., and a further 21% at 70°C.

When the esters collected at 60°C. were treated with urea (24), 12.2% of the material failed to form an adduct. This fraction (NAFD) had the following characteristics: n_D^{20}, 1.47195; iodine number, 180; saponification equivalent, 307; molecular weight (cryoscopy in cyclohexane), 300. The ultraviolet spectrum of NAFD is shown in Fig. 1A and the infrared spectrum in Fig. 2B. For comparison, the infrared spectrum of ethyl esters of unheated linseed oil acids (prepared by alkali-catalyzed ethanolysis and distilled at 0.02 mm.) was also obtained (Fig. 2A).

Hydrogenation of NAFD. A sample of NAFD in ethanol was hydrogenated in the presence of Adams' catalyst. About 2 moles of hydrogen per mole of ester was absorbed. Only 3.3% of the reduced product formed an adduct with urea.

Aromatization and Oxidation, Method I. A mixture of 2.88 g. (9.36 millimole) of NAFD, 11.7 g. (65.7 millimole) of N-bromosuccinimide, and 40 ml. of carbon tetrachloride was stirred at reflux temperature, under nitrogen, for 9 hr. The product, after dehydrohalogenation with 2,4,6-collidine (18), gave 0.50 g. of dark brown oil distilling in the range 148–158°C. (0.02 mm.). The ultraviolet and infrared spectra of this material are shown in Figures 1B and 2E, respectively. The distillate was oxidized by the method of Paschke and Wheeler (18), which involves further treatment with N-bromosuccinimide. Sublimation of the oxidized material yielded only 0.0014 g. of white solid (m.p. 119–126°C.), which was not investigated further.

The use of one mole of N-bromosuccinimide per mole of NAFD with benzene as solvent in the initial bromination (18) did not increase the yield of final product.

Aromatization and Oxidation, Method II. NAFD (2.0 g., 6.5 millimole) was brominated with N-bromosuccinimide (8.1 g., 45.5 millimole), dehydrohalogenated with N,N-diethylaniline, and oxidized with permanganate (8). The aqueous solution resulting from the oxidation reaction was extracted with ether, acidified with hydrochloric acid, concentrated to 175 ml., and extracted with eight 30-ml. portions of ether. The latter ether extracts were dried over anhydrous sodium sulfate and concentrated *in vacuo* to an oil which was sublimed at 0.02 mm. The oily sublimate that collected below 100°C. was discarded; the sublimate that collected at 100–130°C. consisted of white crystalline material on the upper part of the cold finger, and a brown amorphous deposit on the lower part. Resublimation of the white crystals yielded 0.0106 g. (1.1% of theory, based on NAFD) of material melting at 129.3–131.0°C.; mixed m.p. with authentic phthalic anhydride, 131.0–132.4°C.; m.p. of authentic phthalic anhydride in the apparatus employed, 131.6–132.8°C. A portion of the material melting at 129.3–131.0°C. was converted to the imide by heating with urea at 130–135°C. for 20 min. (22). The product, after recrystallization from ethanol-water, consisted of white needles melting at 232.5–234.0°C.; mixed m.p. with authentic phthalimide, 233.7–235.0°C.; m.p. of authentic phthalimide, 234.0–235.0°C.

In a second experiment a 1.28% yield of phthalic anhydride was obtained.

Discussion

The failure of NAFD to form a urea adduct indicates that it has a non-linear structure (24). It was considered possible that non-linearity associated with double bonds contributed to this failure. Hydrogenation of NAFD however yielded a product that still failed to form an adduct. Therefore the non-linearity of the carbon skeleton alone is apparently sufficient to prevent adduct formation.

The infrared spectrum of NAFD (Fig. 2B) has two peaks, at 970 and at 660 cm.$^{-1}$ (10.3 and 15.2 μ), that are not present in the spectrum of the esters of unheated linseed oil acids (Fig. 2A). Both of these peaks, as well as the smaller one at 1650 cm.$^{-1}$ (6.06 μ), are absent in the spectrum of hydrogenated NAFD (Fig. 2D). The spectrum of the adduct-forming distillable esters (Fig. 2C) also exhibits the 970 cm.$^{-1}$ peak but lacks the 660 cm.$^{-1}$ peak. The band at 660 cm.$^{-1}$ is thus a distinguished feature of the spectrum of NAFD.

The absorption at 970 cm.$^{-1}$ is probably due to a *trans* disubstituted double bond (20); that at 660 cm.$^{-1}$, although outside the usual range (729–675 cm.$^{-1}$ [13.71–14.82 μ] [16]), may be due to the C—H out-of-plane deformation of a *cis* disubstituted double bond. A number of compounds that have double bonds in six-membered rings exhibit absorption near 660 cm.$^{-1}$. Cyclohexene has a band at 670 cm.$^{-1}$ (14.97 μ) (1). Bands at 663 and 671 cm.$^{-1}$ (15.1 and 14.9 μ) are characteristic of Δ^2- and Δ^3-steroids, respectively (13). The methyl ester of 2-methyl-α-cyclogeranic acid (23), *cis* α-ionone (6), and *l*-α-phellandrene (19) also absorb in this region. On the other hand, certain steroids with cyclic double bonds in positions other than 2- or 3- lack such absorption (12). Although absorption in this region is not limited to compounds with cyclohexene structures, the band at 660 cm.$^{-1}$ in the spectrum of NAFD may indicate the presence of a double bond in a six-membered ring.

The infrared spectrum (Fig. 2E) of the material obtained from NAFD by bromination and dehydrohalogenation with collidine possesses a band at 747 cm.$^{-1}$ (13.4 μ) that is characteristic of *o*-disubstituted benzene derivatives. A small band at 1597 cm.$^{-1}$ (6.26 μ) and a shoulder at 1480 cm.$^{-1}$ (6.76 μ) are also present; bands of variable intensity in these regions are characteristic of aromatic compounds (2). In the ultraviolet (Fig. 1B) absorption due to aromatic compounds is probably obscured by the strong absorption of conjugated double bonds at 235 mμ. The evidence for an *o*-disubstituted benzene derivative further indicates that at least one compound with an unsaturated six-membered ring structure is present in NAFD.

Direct evidence for the presence of such material is provided by the isolation of phthalic anhydride from the product of the aromatization and oxidation of NAFD. The low yield of phthalic anhydride may indicate that only a small part of the NAFD has the unsaturated six-membered ring structure, or it may indicate that large losses occurred in one or more of the reactions involved. The reasons for the difference in the yields obtained by methods I and II are not apparent. It is possible that method I gives optimal results only when applied to conjugated cyclohexadienes; the lack of significant absorption above 255 mμ in the ultraviolet spectrum of NAFD probably indicates that NAFD contains little or no conjugated cyclohexadiene (25).

Since N-bromosuccinimide is a free radical reagent, the possibility that a free-radical-induced cyclization gave rise to the cyclic precursor of phthalic anhydride during the bromination step cannot be excluded. A mechanism whereby a cyclization of this type might occur has been outlined by Bloomfield (3) in explaining the action of N-bromosuccinimide on rubber. Bloomfield did not isolate any of the proposed cyclic material. If such a cyclization had occurred in the aromatization of NAFD, a higher yield of phthalic anhydride might have been expected from those experiments (aromatization and oxidation, Method I) in which two treatments with N-bromosuccinimide were employed than from those in which N-bromosuccinimide was used only once (aromatization and oxidation, Method II). Higher yields were in fact obtained by Method II.

Summary

The monomeric, non-urea-adduct-forming material from the ethanolysis of heated linseed oil exhibits an infrared absorption band at 660 cm.$^{-1}$ (15.2 μ). This absorption is not present in the spectrum of the esters of unheated linseed oil acids or in that of the adduct-forming esters prepared from heated linseed oil. The monomeric, non-urea-adduct-forming material, on aromatization and oxidation, yielded about 1% of phthalic anhydride, thus providing chemical evidence for the existence in this material of a compound containing an unsaturated six-membered ring.

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Extraction of Corn Oil by Three Petroleum Solvents

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RECOVERY of 99% of the oil in wet-milled corn germs is being obtained industrially by prepressing, followed by extraction with commercial hexane (4). The possibility of direct extraction without prepressing deserves consideration. It also appears desirable to consider the possibility of more efficient extraction by petroleum solvents other than the hexane fraction. In the current work, extraction rates were determined in the laboratory using three petroleum fractions: hexane, heptane, and iso-heptane.

Rate-Extractions

Apparatus. The rate-extraction apparatus employed was a batch, co-current type of laboratory column extractor shown in Figure 1. The equipment was somewhat modified from that shown by Arnold, Sweeney,