

622. *Preparation of Unsaturated Long-chain Alcohols by Means of Lithium Aluminium Hydride : Some Typical Members of the Series.*

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The alcohols corresponding to six naturally occurring fatty acids have been prepared in excellent yields by reduction of the acids or their esters with lithium aluminium hydride.

Nor the least of the difficulties associated with the isolation and purification of the polyethenoid acids of certain fats is the risk—difficult to assess—of their isomerisation during the saponification of the glycerides from which they are derived. As a first step towards a study of these acids, therefore, the possibility is being explored of producing such polyethenoid alcohols, without rearrangement, by direct reduction of the esters with lithium aluminium hydride. Several esters and fatty acids of known constitution have been submitted to such reduction and the yields and purities of the products assessed.

Esters of several fatty acids of wide occurrence have been reduced by previous authors, most

of whom have employed the Bouveault-Blanc procedure. Thus Reid *et al.* (*Org. Synth.*, Coll. Vol. II, p. 468) prepared oleyl alcohol in 82–84% yield from *n*-butyl oleate, and Kass and Burr (*J. Amer. Chem. Soc.*, 1940, **62**, 1797) obtained linoleyl and linolenyl alcohols in 40–50% yields from esters of linoleic and linolenic acids. Better yields were obtained in similar cases by Hansley (*Ind. Eng. Chem.*, 1947, **39**, 55) who used xylene solution and secondary or tertiary alcohols to react with sodium. The Bouveault-Blanc method is not applicable, however, to the reduction of esters containing conjugated unsaturation, *e.g.*, elæostearic ester (a conjugated triene) and ximenynic ester (a conjugated enyne) (Ligthelm and Schwartz, *J. Amer. Chem. Soc.*, 1950, **72**, 1868).

An alternative method is catalytic reduction at high temperatures and pressures as used by Sauer and Adkins (*J. Amer. Chem. Soc.*, 1937, **59**, 1) for the preparation of oleyl alcohol, but the yields are commonly less than 70% and the method is likely to suffer from disadvantages similar to those experienced with the Bouveault-Blanc procedure in the case of conjugated compounds.

It is now reported that the alcohols corresponding to ricinoleic, linoleic, linolenic, α -elæostearic, β -elæostearic, and ximenynic acids can be obtained in excellent yields (*ca.* 90%) by reduction of the acids or esters with lithium aluminium hydride (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197, 2548). In each of the examples studied, as was expected, the only structural change which occurred was the reduction of $-\text{CO}_2\text{R}$ or $-\text{CO}_2\text{H}$ to $-\text{CH}_2\text{OH}$; no reduction of double bonds took place although an excess of lithium aluminium hydride was used in each case. In an attempt to reduce the conjugated enyne group of ximenynyl alcohol to the corresponding diene by further reaction with lithium aluminium hydride no reaction occurred; this behaviour contrasts with the successful reduction of a conjugated enyne containing a non-terminal acetylene group (Chanley and Sobotka, *ibid.*, 1949, **71**, 4140). The ricinoleyl and linolenyl alcohols had properties in agreement with those described in the literature. The melting point of the linoleyl alcohol tetrabromide was somewhat higher (by 5°) than recorded by Kass and Burr (*loc. cit.*), whose statement that the alcohol tetrabromide can be oxidised to the corresponding linoleic acid tetrabromide was confirmed. The α -elæostearyl, β -elæostearyl, and ximenynyl alcohols gave bands in the ultra-violet absorption spectrum characteristic in position and intensity to those from the parent acids, and the β -elæostearyl and ximenynyl alcohols were hydrogenated to octadecan-1-ol. In the case of the α - and β -elæostearyl alcohols the double-bond positions were further confirmed by oxidative degradation to *n*-valeric and azelaic acids. On vacuum-distillation the liquid α -elæostearyl alcohol isomerised to the solid β -elæostearyl alcohol.

EXPERIMENTAL.

Lithium Aluminium Hydride Reductions.—The procedure used was essentially that of Nystrom and Brown (*loc. cit.*), *viz.*: powdered lithium aluminium hydride (usually theoretical amount by weight plus 35–80%)* was refluxed with dry ether for 2 hours with constant stirring, atmospheric moisture being excluded; a solution of the ester or acid, in dry ether, was added at a rate sufficient to cause gentle refluxing; at the end of the addition the refluxing and stirring were continued for a further period (*e.g.*, 30 minutes), followed by cooling in ice-water. The complex was decomposed by the addition of cold 10% aqueous sulphuric acid and the reaction product isolated by ether-extraction in the usual way.

Materials.—The ricinoleic acid was a specimen (>99% pure) kindly given by Dr. F. Hawke of the University of the Witwatersrand; methyl linoleate and linolenate, made by debromination of tetrabromostearic and hexabromostearic acids respectively, were purchased from the Hormel Foundation, U.S.A.; α -elæostearic acid was prepared from tung oil (Hilditch and Riley, *J. Soc. Chem. Ind.*, 1946, **65**, 74) by Dr. D. E. A. Rivett of this laboratory; β -elæostearic acid was obtained by isomerisation of the α -acid with a trace of iodine; ximenynic acid was obtained by the procedure of Ligthelm and Schwartz (*loc. cit.*).

Iodine Values.—The Wijs one-hour procedure was used; the results (I.V.) are expressed as g. of iodine per 100 g. of substance. Somewhat low results were obtained with the non-conjugated alcohols to which this method is applicable; no attempt was made to modify the procedure to obtain theoretical values.

Ricinoleyl Alcohol.—Ricinoleic acid (2.34 g., 0.00785 mol.) and lithium aluminium hydride (0.40 g., 0.0105 mol., *i.e.*, 35% excess) were used. The ethereal solution of the product was washed with 2% aqueous potassium hydroxide to remove any unchanged acid and was then worked up, to give ricinoleyl alcohol (2.06 g., 92.5%) as a colourless, viscous liquid which was free from selective absorption in the ultra-violet region and had $[\alpha]_D^{24} + 5.7^\circ$ (undiluted), b.p. 178°/0.5 mm., n_D^{25} 1.4700, d_4^{25} 0.8999, and $[R_L]_D$ 88.09 (Calc., 87.91) (Found: C, 75.4; H, 12.6%; I.V., 82.7. Calc. for $\text{C}_{18}\text{H}_{36}\text{O}_2$: C, 76.1; H, 12.7%; I.V., 89.4).

* Calc. according to the method of Nystrom and Brown. The fact that small amounts of unreduced acid or ester were present in some preparations after reaction may have been caused by consumption of hydride by traces of moisture in the ether and apparatus or to lack of purity of the hydride itself.

Hydrogenation of Ricinoleyl Alcohol.—Hydrogenation in ethyl alcohol solution in the presence of palladium–calcium carbonate yielded octadecane-1 : 12-diol, m. p. 79.5–80° (from ethyl alcohol) (Shinozaki and Yubo, *J. Agric. Chem. Soc. Japan*, 1937, **13**, 18, record m. p. 71.2°, $[\alpha]_D^{25} + 5.3^\circ$ (in ethyl alcohol) [Found : 0.5977 g. took up 46.8 c.c. of H_2 (N.T.P.). Calc. for $C_{18}H_{36}O_2$: 47.1 c.c. H_2].

Linoleyl Alcohol.—Methyl linoleate (5.88 g., 0.020 mol.) and lithium aluminium hydride (0.55 g., 0.0145 mol., *i.e.*, 45% excess) were used. The product (5.3 g.) was distilled at 0.5 mm. through a 6 inch column packed with Berl saddles, giving (a) b. p. 144–145° (3.0 g.), (b) b. p. 146–146° (0.75 g.), and (c) b. p. 146–147° (1.25 g.). Carbon and hydrogen analyses indicated that (b) and (c) were substantially pure linoleyl alcohol, whereas (a) contained some unchanged ester; hydrolysis of (a), followed by removal of free fatty acid, showed that 9.5% of linoleic ester was present, the final yield of alcohol being therefore 89% plus some amount (*ca.* 4–5%) accounted for by distillation hold-up. The alcohol gave n_D^{25} 1.4678, d_4^{25} 0.8588, $[R_L]_D$ 86.06 (Calc. 85.92) and $E_{1\text{cm}}^{1\%}$ 0.10 at λ_{max} . 232 μm ., corresponding to *ca.* 0.01% of conjugated diene present [Found : C, 81.0; H, 13.1%; I.V., 187. Calc. for $C_{18}H_{34}O$: C, 81.15; H, 12.85%; I.V., 191]. The alcohol was characterised by the preparation of its solid tetrabromide, m. p. 93°, in 28% yield (Kass and Burr, *loc. cit.*, record a 48% yield of material, m. p. 88°) which was oxidised by permanganate to 9 : 10 : 12 : 13-tetrabromostearic acid* (m.p. and mixed m. p.) following the procedure of Kass and Burr but using a shorter reaction time (60 minutes).

Linolenyl Alcohol.—Methyl linolenate (5.8 g., 0.0198 mol.) and lithium aluminium hydride (0.55 g., 0.0145 mol., *i.e.*, 46% excess) gave a colourless oil (5.03 g.) which readily oxidised in air (Found : C, 81.55; H, 12.4%; I.V., 277. Calc. for $C_{18}H_{32}O$: C, 81.75; H, 12.2%; I.V., 288) containing very little unchanged ester, since, after hydrolysis of a 4.90-g. sample, 4.77 g. were recovered as non-acidic material; the yield of alcohol recoverable was therefore 93.5%. The alcohol had b. p. 142°/0.4 mm., n_D^{25} 1.4775, d_4^{25} 0.8708, $[R_L]_D$ 85.64 (Calc. 85.45), and $E_{1\text{cm}}^{1\%}$ 8.4 at λ_{max} . 234 μm ., corresponding to *ca.* 0.84% of conjugated diene present (doubtless arising from autooxidation of the sample; cf. Farmer, Koch, and Sutton, *J.*, 1943, 541). The alcohol was characterised by the preparation of its solid hexabromide, m. p. 170°, in *ca.* 20% yield (Kass and Burr, *loc. cit.*, record a 25% yield and m. p. 171–172°) (Found : Br, 64.25. Calc. for $C_{18}H_{30}OBr_6$: Br, 64.45%). The phenylurethane, 3 : 5 dinitrobenzoate, and α -naphthylamine complex of the latter were oils.

α -Elæostearyl and β -Elæostearyl Alcohols.— α -Elæostearic acid (13.9 g., 0.05 mol.) and lithium aluminium hydride (2.36 g., 0.063 mol.; *i.e.*, 70% excess) were used. The product, in ethereal solution, was washed with aqueous sodium carbonate solution and worked up in the usual way, yielding a slightly yellow oil (10.88 g., 82.5%) which solidified below 25°; the somewhat low yield was attributed to the formation of stable emulsions during the alkaline washing. The oil, α -elæostearyl alcohol, gave on ultra-violet examination, $E_{1\text{cm}}^{1\%}$ 1310, 1730, 1334 at λ_{max} . 261, 270.5, and 281 μm ., respectively (in ethyl alcohol); on distillation (b. p. 150–154°/0.2 mm.) a solid β -elæostearyl alcohol was obtained, having m. p. 58.5–59.5° after recrystallisation from *iso*heptane; this gave, on ultra-violet examination, $E_{1\text{cm}}^{1\%}$ 1493, 1996, 1529 at λ_{max} . 258, 268.5, and 279 μm ., respectively (in ethyl alcohol) (Found : C, 81.1; H, 12.8%. $C_{18}H_{32}O$ requires C, 81.75; H, 12.2%). The positions and intensities of the ultra-violet absorption bands of the oil (before distillation) and the solid of m. p. 58.5–59.5° correspond fairly closely to those for α - and β -elæostearic acids respectively [O'Connor and Heinzelman, *J. Amer. Oil Chem. Soc.*, 1947, **24**, No. 6, 212, record that the central bands of α - and β -elæostearic acids have $E_{1\text{cm}}^{1\%}$ 1686 at λ_{max} . 270 μm . and $E_{1\text{cm}}^{1\%}$ 2161 at λ_{max} . 268 μm ., respectively (in ethyl alcohol solution)].

Oxidation of α -Elæostearyl Alcohol.—A sample (2.96 g.) of the oil obtained above (before distillation) was oxidised with potassium permanganate by Farmer and Brown's method (*J.*, 1935, 761) except that the oil was dissolved in a small quantity of acetone before adding the permanganate solution (in order to obtain a fine dispersion). The steam-involatile portion of the product (0.5 g.) was recrystallised from dilute aqueous hydrochloric acid, to give azelaic acid, m. p. 101.5–103° [Found : A.V. (in mg. KOH per g.), 600. Calc. for $C_9H_{16}O_4$: A.V., 596], giving no depression of m. p. on admixture with an authentic sample of m. p. 106°. The steam-volatile portion (b. p. 177°/655 mm.) of the product was converted into the *p*-bromophenacyl ester, m. p. 62°, which gave no depression on admixture with an authentic specimen of the ester of *n*-valeric acid (m. p. 63–63.5°). A similar permanganate oxidation of the solid β -elæostearyl alcohol also yielded azelaic and *n*-valeric acids.

Hydrogenation of β -Elæostearyl Alcohol.—Hydrogenation of β -elæostearyl alcohol in ethyl alcohol in the presence of Adams's catalyst yielded octadecan-1-ol, m. p. 57.5–58°, undepressed on admixture with an authentic specimen of m. p. 57.5–58.5° [Found : 0.0985 g. took up 25.0 c.c. H_2 (N.T.P.). Calc. for $C_{18}H_{32}O$: 25.1 c.c. H_2].

β -Elæostearyl Alcohol from β -Elæostearic Acid.— β -Elæostearic acid (0.947 g., 0.00328 mol.) and lithium aluminium hydride (0.215 g., 0.00567 mol., *i.e.*, 130% excess) gave a product (0.782 g., 87%), m. p. 56–57°, when worked up as for the α -alcohol. After two recrystallisations from *iso*heptane, the m. p. rose to 58.5–59.5°. The alcohol had $E_{1\text{cm}}^{1\%}$ 1528, 2095, and 1654 at λ_{max} . 258, 268, and 279 μm ., respectively (in ethyl alcohol).

Ximenynyl Alcohol.—Ximenynic acid (1.39 g., 0.005 mol.) and lithium aluminium hydride (0.261 g., 0.0069 mol., *i.e.*, 84% excess) were used. After washing of the ethereal solution of the product with 5% aqueous potassium carbonate solution and then working up in the usual way, *ximenynyl alcohol* (1.35 g., 97%) was obtained as a colourless liquid which solidified on cooling. The product was distilled (b. p. 172–175°/1 mm.). The main fraction, once recrystallised from light petroleum (b. p. 50–60°), had m. p. 26–27°, rising to m. p. 30–31° on further recrystallisation, n_D^{25} 1.4790, n_D^{40} 1.4726, $E_{1\text{cm}}^{1\%}$ 591.5 at λ_{max} . 229 μm . (in cyclohexane) (Found : C, 81.9, H, 12.2. $C_{18}H_{32}O$ requires C, 81.75; H, 12.2%);

* Geneva numbering.

ximenynic acid gives $E_{1\text{cm}}^{1\%}$ 583 at λ_{max} 229 m μ . (in cyclohexane). The *a-naphthylurethane*, m. p. 57—57.5° (from light petroleum) (Found : C, 80.35; H, 9.05. $\text{C}_{25}\text{H}_{39}\text{O}_2\text{N}$ requires C, 80.3; H, 9.05%), and *phenylurethane*, m. p. 69—69.5° (from light petroleum) (Found : C, 78.45; H, 10.05. $\text{C}_{25}\text{H}_{37}\text{O}_2\text{N}$ requires C, 78.3; H, 9.7%), were prepared.

Attempted Reaction of Ximenynyl Alcohol with Lithium Aluminium Hydride.—Ximenynyl alcohol (0.6 g., 0.0025 mol.) was refluxed in dry ether with lithium aluminium hydride (0.1 g., 0.00263 mol.) for 2 hours. The product had the same ultra-violet spectrum as the original ximenynyl alcohol.

Hydrogenation of Ximenynyl Alcohol.—Hydrogenation in ethyl alcohol in the presence of palladium-calcium carbonate yielded octadecan-1-ol, m. p. 58.5—60°, not depressed on admixture with an authentic specimen of m. p. 59—60° [Found : 0.01399 g. took up 3.62 c.c. of H_2 (N.T.P.). Calc. for $\text{C}_{18}\text{H}_{32}\text{O}$: 3.56 c.c.].

The authors thank Dr. W. S. Rapson for his interest in this work, Mr. D. J. S. Gray and Mr. F. W. G. Schöning for carrying out the microanalyses, and the South African Council for Scientific and Industrial Research for permission to publish this paper.

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[Received, July 3rd, 1950.]
