Characterization of Lipids Extracted from Pickled Lambskins by a New Industrial Degreasing Process

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In the manufacturing of leather from lambskins, skin degreasing is an important preliminary stage in which excess fats are removed. A new solvent-phase degreasing process, which leads to a complete recovery of extracted fats, has been studied and scaled up in our laboratory. In this paper, we study the characteristics of these extracted fatty substances that have not been reported previously. Extracted fats which, up to now, were considered waste, can be used. Different methods have been proposed for their possible utilization.

KEY WORDS: Characterization, degreasing, extraction, fat-liquoring, fatty substances, lambskins, lipids, pickled skins, trichloro-trifluoro-ethane, utilization.

In the leather industry, tannery manufacturing consists of transforming raw hides into finished leather through various mechanical and chemical operations. In the processing of small skins (goats, pigs, sheep), degreasing of pickled skins is an important operation that affects the quality of the final products. Excess fats must be removed before tanning and dyeing operations in order to obtain a good quality of leather.

Pickling is a process in which hides are acidified in order to make their preservation possible for storage and transport and to make degreasing easier through decomposition of protoplasmic membranes of cellular fats. Pickled skins have a water content of 55–60% by weight and are acid (pH of the aqueous phase contained in hides is between 1 and 2).

Fat content in lambskins is generally high but many variations are observed depending on the country of origin, type of farming, and age and sex of the animals. Lambskins originating from England, New Zealand and Australia traditionally contain a high percentage of fat (37% of dry material weight) while the fat content of hides coming from Germany, the Netherlands and France ranges from 10 to 17%. Skins from Tchad, Niger and North Africa are even lower (less than 4%) and do not require degreasing (1).

After degreasing, an experimental range from 3 to 8% fat content leads to good quality leather. Skin degreasing appears to be an important operation.

In the traditional degreasing process in aqueous medium, fats are emulsified in the presence of an anionic or nonionic surfactant and solvent (light petroleum rich in hexane). A single stage is not sufficient to obtain high efficiency and consequently this operation is time-demanding. Another disadvantage of the process lies in the pollution of the environment. Effluents contain high pollutant loads that are only partially, or not at all, recycled. The extracted fat is not recovered.

A new degreasing process has been studied in our laboratory and scaled up for industrial manufacturing (2). It can solve both the problem of efficiency in the degreasing of pickled skins and the water pollution problem. Fats are extracted in the presence of trichloro-trifluoro-ethane (TTFE), which is efficient without using a surfactant. The solvent is separated by distillation and recycled. No aqueous effluent is discarded. Recovered fatty substances are free of impurities.

In this study, we compare the composition of fats obtained to that of fats extracted with hexane, the solvent commonly used for lipid extraction. The influence of temperature on fat characteristics is also considered.

EXPERIMENTAL PROCEDURES

Fat extraction. Laboratory experiments were carried out in a one-liter reactor with stirring at room temperature for one hour, then at 40°C for 30 min. Pieces of lamb-skin (2 × 3 cm sides, pH of aqueous phase 1–2, water content 55–60% by weight) were introduced into the reactor with solvent. The reaction medium was then filtered in order to separate pieces of hide from the liquid phase. Fats were recovered from the liquid phase by evaporation under reduced pressure (16 mm of Hg) and were analyzed.

Extractions in the industrial unit were carried out in an appropriate reactor with stirring at room temperature with 1000 kg of pickled skins. At the end of the working cycle, solvent was separated from fats by distillation under atmoshperic pressure (final temperature 90°C). Samples of extracted fats were recovered and analyzed.

Characterization and analysis of fats. Viscosity of extracted fats was determined in a falling sphere viscosimeter according to DIN 3015 (Deutsche Industrie Norm). Iodine, acid and saponification values, iodine color value, unsaponifiable material, oxidized acids, mineral ash and phospholipid content were determined according to experimental procedures described in AFNOR (Association Française de Normalisation) (3). The constituents of unsaponifiable material were identified by thin-layer chromatography according to AFNOR 60232 (silica gel on aluminium support, eluent benzene/acetone, 95:5, spots visualized by means of dichlorofluorescein).

Fatty acid composition was determined by gas chromatography (Carlo Erba, Milano, Italy; CG 6000). Fats were analyzed after transesterification to methyl esters (4) under the following conditions: carbowax capillary column 50 m × 0.32 mm I.D; helium as carrier gas (40 kPa pressure); air pressure 100 kPa, hydrogen pressure 50 kPa; injector at ambiant temperature; detector temperature at 220°C; and programmed oven temperature from 50 to 180°C at 10°C/min.

RESULTS AND DISCUSSION

Extraction yield and main characteristics of fats extracted with TTFE and hexane are compared in Table 1. A higher quantity of lipids was extracted by TTFE, but the characteristics of the extracted fats were similar. This result was also reported by Temple (5) in the extraction of soybean oil, where the quantity of phospholipids ex-

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TABLE 1

Comparison Between Characteristics of Fats Extracted by TTFE and Hexane

	Fat content g/kg pickled hide	Unsaponifiable (%)	Ashes (%)	% Fatty acid composition						
				C_{14}	C_{16}	$C_{16:1}$	C_{18}	$C_{18:1}$	$C_{18:2}$	C_{20}
TTFE	99	11.2	0.29	3.3	20.2	3.6	19.4	39.4	1.2	1.6
Hexane	66	10	0.16	2.9	19.9	3.3	20.5	38.1	1.6	1.7

tracted by TTFE is slightly higher than by hexane, but the iodine and acid values and fatty acid compositions were quite similar. Vos (6) and Ferrick (7) drew the same conclusion after comparing TTFE with other solvents used in lipid extraction. Characteristics of fats recovered after an industrial degreasing operation are similar to those of a fresh skin except that the acid value is higher, 8–20, than the value of 2 for fresh skin (8).

Differences can be noted between lipids of fresh hides and tallow. Tallow contains a lower quantity of unsaponifiable materials and has a higher melting point. Variations of characteristics observed can be partly explained by fluctuations in the lipids due to farming or feeding of the ovines and by storage of the pickled hides. Lipids of pickled skins are modified during storage with free fatty acids being formed by hydrolysis.

A sample of these fats was dissolved in TTFE and successive extractions were carried out with water. Acidity of the recovered fats was found unchanged. We believe that this indicates that this acidity is essentially organic and cannot be linked to the presence of residual mineral acids (sulfuric acid) used during the pickling treatment.

Because of pickling and prior treatments (especially dehairing), various mineral ions are present in hides. These salts are partly removed with fats during extraction. Fats derived from pickled skins contain 0.14% of mineral ash, but if skins are washed before extraction the percentage is only 0.004%.

Variation in density (0.93 to 0.95) can be attributed to variation in the amount of unsaturated lipids as determined by iodine value (IV) and the average molecular weight as determined by saponification value (SV). An average density can be estimated by a general equation proposed by Lund (9): $d = 0.8467 + 0.00013\ SV + 0.00014\ IV$, and is similar to the experimental value. Viscosity is 6–6.5 stokes; it also depends on the carbon chainlength (SV) and, more particularly, on the quantity of unsaturated compounds (I.V) since it decreases almost linearly with an increase in iodine value. SV and IV varies from 180 to 190 and from 50 to 52, respectively.

The content of unsaponifiable material can be as high as 25%. As is the case with fresh skins, the amount of unsaponifiable material depends on the origin of the skins, the type of farming and feeding of the ovines. The content in skins coming from North America is only 2%, but it can be as high as 25% in skins from Australia (10). The amount of cholesterol can be as high as 80% in the unsaponifiable fraction. Cholesterol, phospholipids and glycolipids are the main lipid components of cellular membranes. Unsaponifiable components are present in lower layers of the epidermis, but their transport from one structure or one membrane to another and from one layer to another can take place by a single contact (11). Moreover, unsaponifiable material is rather stable despite the drastic treatment involved in skin processing before degreasing (12). Thin-layer chromatography was used to identify the main components of unsaponifiable material. Four groups of products were successively eluted: carotenoids (Rf = 0.05); sterols (Rf = 0.23, cholesterol standard); fatty alcohols (Rf = 0.7, cetyl alcohol standard); saturated or unsaturated hydrocarbons (Rf = 0.9, squalene standard).

Phospholipid content was high in fresh skins (about 20%) and can be as high as 40% in the epidermis (13). The very low percentage (0.02%) observed in fats of pickled skins suggests that they decompose and are eliminated during acidic or basic treatment in processing of skins (dehairing, pickling, etc.).

Results of quantitative and qualitative analysis of fats indicate that palmitic (22–23%), stearic (19–20%) and oleic (42–44%) acids are the major components and their total amount is 85%. Similar ratios are found in fresh or pickled lambskins.

The fatty acid compositions of total, neutral (glycerides) and acid lipids showed that acid lipids contain about 7% more saturated fatty acids (myristic, palmitic and stearic) than total lipids. We believe that this can be explained by the preferential location of saturated acids in α and α' sites in glycerides. The hydrolytic cleavage in the presence of acid (pickling) initially proceeds at these sites (14).

In industrial units unlike laboratory runs, fats are recovered after distillation at a rather high temperature (90°C). Because the characteristics of fats can be influenced by high temperature, the physical constants were determined and analyzed after evaporation at room temperature. In all cases, runs were carried out with hides with similar characteristics and with the same time of storage after the pickling operation. The fatty acid composition showed the same major components: palmitic acid (24%), stearic acid (23%), and oleic acid (41%). Fat extracted at high temperature is dark yellow; its color value is 4 instead of 2.5 for fat extracted at room temperature. The amount of oxidized acids in fats after heating at various temperatures has been determined. Its increase is proportional to the temperature of distillation (it is 0.9–1% at ambient temperature and 5.6% at 90°C). Oxidation of unsaturated compounds leads to peroxides, hydroxy acids and other by-products, which catalyze peroxidation of adjacent chains (14).

The amount of unsaponifiable material is lower when fats are distilled at ambient temperature (15%). This decrease can be attributed to by-products from oxidation. Similar results were reported by Gavend (15). After heating, both the Lea value (related to oxidation) (16) and the amount of unsaponifiable matter increase.

The characteristics of the fatty substances extracted with TTFE are similar to those extracted with hexane.

These fats cannot be utilized for animal feeding because of their high content of free fatty acids and unsaponifiable material. Nevertheless, they seem to be attractive as starting materials for the production of fatty acids (soaps, cosmetics) and additives for lubricants.

Finally, their utilization in leather processing itself appears to be interesting. The stage of fat-liquoring, which consists of a controlled introduction of uniformly dispersed compounds into leather, must be carried out before any intermediate or final drying operation takes place. Recent work in our laboratory has been done on the appropriate composition of this liquor.

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