caprylic acid. *C. carthagenensis* provides an oil richer in both lauric and capric acids than coconut oil. Only from the original sample of *C. llavea* has the major component been isolated and rigorously characterized by derivative formation (13). However, the GLC data indicating the presence of these saturated acids in the closely related species leave little doubt as to their identity.

Any of the oilseeds from the five species reported here should be amenable to present processing methods of oil recovery and preparation of intermediate chain-length acids from the glycerides. A recent patent demonstrates one procedure for preparing decanoic acid from *C. llavea* oil (9). These oils should find ready acceptance by industry if suitable strains of *Cuphea* can be found or agronomically developed to permit production of the seed economically enough to make the oil available at a competitive price.

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[Received August 5, 1963—Accepted November 27, 1963]

Recent Research on Sesamin, Sesamolin, and Related Compounds[1]

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Abstract

This review covers the literature on sesamin, sesamolin and related compounds published since 1951. The topics reviewed include structural considerations, natural occurrence, influence of oil processing, analytical methods, isolation procedures and commercial preparations, various biological effects and stability questions.

Recent developments in pyrethrum synergists are discussed at length, since they owe so much to the discovery of the synergistic activities of sesamin and sesamolin.

Introduction

THE SEED OIL OF *Sesamum indicum*, commonly known as sesame oil, contains two minor constituents, sesamin and sesamolin, which are responsible for its characteristic color reactions, its insecticidal synergism and some other specific properties. Sesamol, a phenolic antioxidant, usually present in traces, is formed from sesamolin under certain processing conditions.

A critical survey of the literature on sesamin, sesamolin and sesamol was included in a 1951 review on sesame oil (1). The purpose of the present paper is to review work carried out since then on these and related compounds.

Structural Considerations

Sesamin is 2,6-(3,4-methylenedioxyphenyl)-*cis*-2,7-dioxabicyclo-[3.3.0]octane. Its synthesis has been reported from three laboratories (2–4). According to its formula, three stereoisomers are theoretically possible, each existing in two enantiomorphic forms. Sesamin and asarinin constitute two members of this series. The third member was discovered recently by Beroza (5) and termed epiasarinin by him. The structures of these compounds have been elucidated (5–8) and absolute configurations assigned to them as shown in Figure 1.

Recent nuclear magnetic resonance measurements on sesamin and asarinin led Govil, Kanekar, and Khetrapal (9) to suggest that the structures assigned to sesamin and epiasarinin should be interchanged. In the course of a study of the stereochemistry of some new lignanes carried out about the same time, Weinges (10) also measured the NMR spectra of sesamin and asarinin. His results confirmed the previously established configurations. Becker and Beroza (11) used the same technique not only on sesamin and asarinin, but also on epiasarinin, and similarly found no reason to alter the conclusions assigning to these three stereoisomers the structures shown in Figure 1.

The structure of sesamolin has been established as that of 2-(3,4-methylenedioxyphenoxy)-6-(3,4-methylenedioxyphenyl)-*cis*-3,7-dioxabicyclo [3.3.0] octane (Fig. 2a), with the same tetrahydrofurfurofuran nucleus as in sesamin (8,12,13). Sesamolin differs from sesamin by the presence of a connecting oxygen atom between the tetrahydrofurfurofuran nucleus and one of the methylenedioxyphenyl groups. This makes sesamolin an acetal-type derivative of sesamol (Fig. 2b), as suggested earlier by Boeseken, Cohen and Kip

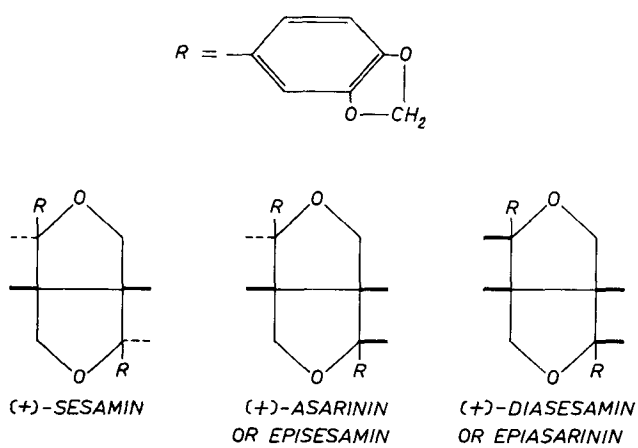

FIG. 1. Absolute configuration of the dextrorotatory stereoisomers of the sesamin series (6).

[1] Contribution from the National and University Institute of Agriculture, Rehovot, 1963, Series No. 566-E.

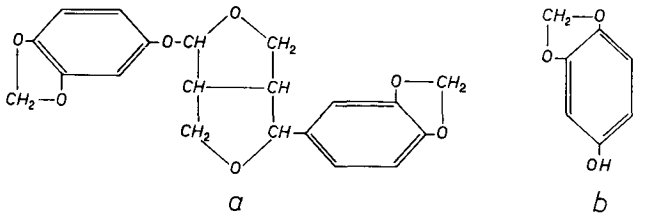

FIG. 2. Structures of sesamolin (a) and sesamol (b).

(14). No diastereoisomer of sesamolin has been reported. It is strange to note that *samin*, a crystalline dextrorotatory compound having the formula $C_{13}H_{14}O_5$ and which is formed upon removal of sesamol from sesamolin by dilute mineral acids, does not appear to have been investigated since its isolation by Adriani (15) in 1928. In view of the recent elucidation of the structure of sesamolin referred to above, samin is probably a hemiacetal (12) (Fig. 3).

A new compound, closely related to sesamin, was discovered recently by Jones, Beroza, and Becker (16) in the seed oil of *Sesamum angolense*, a wild sesame from Northern Rhodesia. This compound, named sesangolin by these authors, was shown to be 2-(3,4-methylenedioxyphenyl)-6-(6-methoxy-3,4-methylenedioxyphenyl)-cis-3,7-dioxabicyclo [3:3.0] octane (Fig. 4).

Natural Occurrence

Sesamin has been isolated from the bark of various *Fagara* species (3b, 8,17–19), from *Chamaecyparis obtusa Sieb* (20) and *Ocotea usambarensis Engl.* (21), from the heartwood of *Gingko biloba* (22,23) and the bark of *Flindersia pubescens* (24), from *Evodia micrococca*, var. *pubescens* (25) and from the fruit of *Piper guineense* (26). Earlier known compounds have been identified with sesamin. Thus, fagarol is d,l-sesamin (8,18) and pseudo-cubebin has turned out to be d-sesamin (21,26).

In 1951, a report appeared claiming that the seed oil of *Sesamum angolense* contained as much as 9% sesamin (27). This figure was based on the insecticidal synergism of the oil with pyrethrins. The work by Jones et al. (16) has shown, however, that no sesamin is present and that the high synergistic activity of the oil can be accounted for by the presence of sesamolin and sesangolin.

Unlike sesamin, sesamolin has not been found to occur in any genera other than *Sesamum*, nor has sesangolin been reported in any *Sesamum* species other than *S. angolense*.

Sesamin and sesamolin appear in the seed of *Sesamum indicum* concurrently with oil formation (28). They are not found in the vegetative parts of the plant (28). Beroza and Kinman (29) have presented a detailed study of the influence of strain, location grown, aging and frost damage on the sesamin, sesamolin and sesamol content of the oil of sesame seeds. Only differences in sesamin content due to strain were significant. Frost damage decreased both sesamin and sesamolin contents.

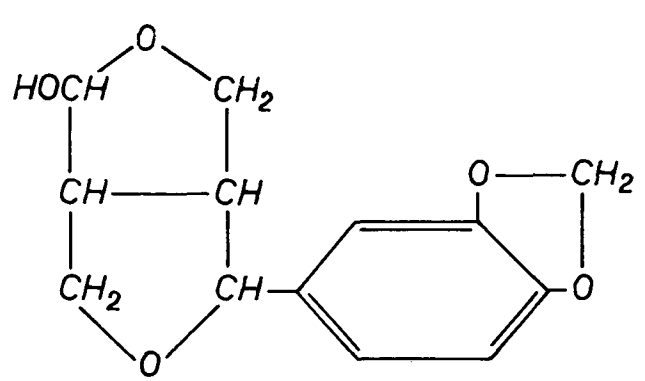

FIG. 3. Probable structure of samin.

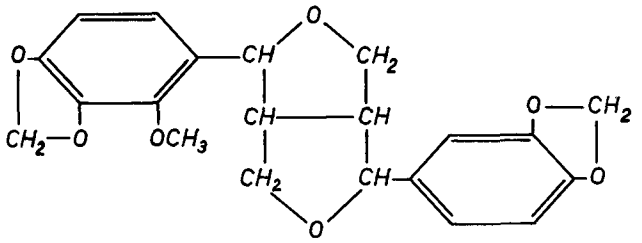

FIG. 4. Structure of sesangolin (16).

Influence of Processing

The influence of extraction and processing on the content of sesamin, sesamolin and sesamol of sesame oil has been studied by Fugimura and Toyama (30). Bhide and Kane (31) have reported on the effect of processing on the Baudouin color test, i.e., on sesamolin and sesamol content. Different bleaching earths may give similar reductions in oil color but cause widely different adsorption of sesamolin (32). Hydrogenation of sesame oil partially decomposes sesamin and sesamolin (33). The great sensitivity of sesamolin towards processing presents a serious problem in those countries where sesame oil is a mandatory indicator substance for margarine or hydrogenated vegetable oils (vanaspati), since the prescribed color test is caused by sesamolin and free sesamol. This problem will be discussed below.

Detection and Determination

The history of the color reactions given by sesame oil and its minor constituents was reviewed in 1951 (1). The test most widely used is the one proposed by Villavecchia and Fabris, which yields a cherry-red color when sesame oil is shaken with concentrated HCl in the presence of furfural. This reaction is caused by the presence of sesamolin or free sesamol in the oil. Because of its legal implications as an identification test, it has gained great importance in the past. But since sesamolin and sesamol are strongly affected by processing conditions, the test can hardly be expected to be reliable, and this has been the main objection to its use (34–37). Azo- and coal-tar dyes interfere with the test and must be removed (38,39). In order to increase the reliability of the test in the detection of fatty adulterants, Daghetta and Bruss (40) made the logical suggestion of using synthetic sesamol in place of sesame oil as an indicator. It appears, however, that sesamol esters or other more stable derivatives (41) might be better suited for this purpose.

Another color test, originally proposed by Pavolini (42) and studied in detail by Pavolini and Isidoro (33), consists in the formation of a brilliant red color turning blue-green, when sesame oil or sesamin are allowed to react with a mixture of sulfuric acid, acetic anahydride, and furfural. The test has been stated to be superior to the Villavecchia and Fabris test (43–45) because it is more sensitive and also because sesamin is less affected by processing conditions than sesamolin.

With the discovery of the synergistic insecticidal properties of sesamin, sesamolin and other compounds containing the 3,4-methylenedioxyphenyl structure, the problem of determining or identifying the individual compounds has become important.

A method for the determination of sesamol, sesamolin, and sesamin in sesamin concentrates and in oils has been published by Suarez et al. (46). This procedure, similar to one described earlier (47), involves the extraction of sesamol into aqueous alkali, the separate determination of sesamol and sesamolin by color reaction with furfural and aqueous sulfuric acid, and the determination of sesamin by spectrophotometric absorption measurements, with a correction for the sesamolin present.

These methods fail when other synergists are present. The methylenedioxyphenyl group common to all these compounds can be assayed by color development with gallic-sulfuric acid (48) or with chromotropic-sulfuric acid (49,50). However, in order to identify individual compounds, chromatographic techniques are required.

Beroza (51) described a procedure for the separation of pure sesamin by chromatography on a silicic acid column, followed by quantitative UV absorption measurements. A reversed-phase paper chromatographic method was devised by the same author (52) for the identification of sesamin, sesamolin, and the usual commercial synergists. More recently, Beroza (53) developed a TLC procedure for the rapid identification of all commercial 3,4-methylenedioxyphenyl synergists, as well as sesamin and sesamolin. The compounds are separated on silicic acid plates and made visible by spraying with furfural-sulfuric acid or, preferably, with chromotropic-sulfuric acid. R_f values, as well as the color of the spots, are useful for identifying the various compounds.

Isolation Procedures and Commercial Preparations

Sesamin was isolated by laboratory-scale molecular distillation of sesame oil (54). A similar procedure also yielded sesamolin (55). Details for obtaining pure sesamin and sesamolin by extraction from sesame oil have been given by Haslam and Haworth (13) and by Beroza (56).

A number of patents have been granted relating to the extraction of "sesamin concentrates" for use as pyrethrin synergists. The solvents used are methanol (57), aqueous acetone (58), chilled petroleum ether (59), acetonitrile (60) and gamma-butyrolactone (61). The concentrates obtained contain a mixture of sesamolin and sesamin. Data on their composition have been presented by Suarez et al. (46).

Synthetic sesamol has been gaining importance as a potential indicator for margarine and hydrogenated vegetable fats, as a possible antioxidant, and as a starting material for the preparation of insecticidal synergists. Its synthesis from the corresponding amine has been described (62). Patents have been granted recently for the synthesis of sesamol and its esters or ethers, starting from piperonal (41,63,64). Beroza (65) has given details for the laboratory synthesis of sesamol from piperonal.

Synergism with Pyrethrum Insecticides

Pyrethrum is highly valued as an insecticide because it produces rapid knock-down, i.e., paralysis, and because it exhibits a low degree of toxicity in mammals. Its cost of production, however, is high and pyrethrum would lack commercial significance were it not for the boosting influence of the synergists with which it is usually formulated. Pyrethrum-synergist combinations do not evoke the high degree of resistance commonly encountered with most synthetic insecticides. Although insecticidal toxicity is enhanced by the synergist, toxicity towards mammals is not increased.

The role played by sesame oil in the early development of pyrethrum synergists is now well known. The discovery (66) that sesamin is a synergist and that its activity is due to its methylenedioxyphenyl groups triggered an intensive search for more active adjuvants containing this group. Of the many hundreds of compounds prepared, some have found commercial application. The first successful compounds were piperonyl butoxide, sulfoxide, piperonyl cyclonene (originally named piperonyl cyclohexenone) and *n*-propyl isome. Such compounds have largely superseded sesame oil or sesamin concentrates as adjuvants, although the latter still continue to find limited application (57–61,67–71).

Subsequently, little progress was made in the field of pyrethrum synergists until 1954, when the search for more effective adjuvants again received a boost, and again sesame oil was involved. In that year, Beroza (56) reported that sesamolin, isolated from sesame oil, was about five times as potent as sesamin, when tested as a synergist for pyrethrin against houseflies. The probable synergistic activity of sesamolin had already been suggested earlier (1). As a result of Beroza's discovery, a great number of compounds derived from sesamol, i.e., containing the 3,4-methylenedioxyphenoxy group, were synthesized (65, 72–81). The most active among them appear to be the acetals (73–75). Sesamol itself is inactive (82,83). In the U.S., synergists prepared from sesamol are covered by four patents (84–87).

Sesangolin, a natural synergist recently discovered in the oil from *Sesamum angolense* (16), is about as active as sesamin.

Strangely, the very considerable amount of work spent on the synthesis and screening of many new compounds does not seem to be commensurate with the knowledge gained regarding the relation between chemical structure and adjuvant activity. The superiority of methylenedioxyphenoxy compounds over the corresponding methylenedioxyphenyl derivatives, as illustrated by sesamolin and sesamin, respectively, has been established (65). Moore and Hewlett (81) state than in addition to a methylenedioxyphenyl group with an unsubstituted methylene, a short lipophylic side chain is required. Stereoisomers seem to differ little in synergistic activity: a slight superiority of sesamin over asarinin has been noted (88), epiasarinin being the least active of the three. Optical antipodes are equally effective.

The following are some of the more successful synergists developed in recent years. Sulfone (89,90) exhibits an activity similar to that of the older sulfoxide from which it is derived. Bucarpolate (91) is a representative of the group of 3,4-methylenedioxybenzoate esters. Sesamex, also known under the trade name Sesoxane is 2-(2-ethoxyethoxy)ethyl 3,4-methylenedioxyphenyl acetal of acetaldehyde. This compound is a highly successful synergist for allethrin, cyclethrin and pyrethrins (92,93), barthrin (94), methoxychlor (95–97), malathion (98), SD-3562 (99) and carbamate insecticides (100–103). Sesamol benzenesulfonate is a powerful synergist for pyrethrin and allethrins (74,81,84,104) as well as

for carbamate insecticides (102). Finally, mention should be made of the group of N-substituted carbamates of sesamol. Compounds of this type are pyrethrin synergists (105–107), or they may be toxic by themselves: thus, sesamol methyl carbamate has been reported to be very toxic to the housefly and other insects (108).

Some progress in the elucidation of the mechanism of action of synergists has been made. Sesamex was shown to inhibit the enzymatic oxidation of *p*-nitrophenyl-N-methyl-N-hydroxymethylcarbamate (109), both in microsomal systems and in the housefly. The above compound is a metabolite of *p*-nitrophenyl-N,N-dimethyl carbamate. One possible explanation for the action of synergists, at least in the case of carbamates, seems to be their interference with the metabolic degradation of the toxic compounds.

Other Biological Effects

Sesame oil is a preferred vehicle for oily medications, and it has occasionally been suspected of causing physio-pathological effects. Among these may be mentioned an increase in the hematocrit of rats (110), increased oxygen uptake of tissues (111–113), lesions of the parenchyma (114) and production of sarcomas (115). It is not clear to what extent these effects can be ascribed to some specific constituent of sesame oil. It has been pointed out, e.g., that many oils cause tissue malignancy, following injection (116).

Bishoff's work (117–119) on the cocarcinogenic action of sesame oil and certain cholesterol oxidation products deserves special consideration, in view of the intrinsic importance of the subject. In an extensive review on carcinogenesis through cholesterol and derivatives (120), Bishoff points out that there is no evidence that sesame oil, used as a vehicle for parenteral administration in rats or mice, is carcinogenic. Bishoff mentions, as a possible exception, excessively heated or peroxidized sesame oils. The cocarcinogenic action of sesame oil, according to Bishoff, derives from the fact that certain oxidation products of cholesterol are highly carcinogenic when administered in sesame oil, noncarcinogenic when administered in aqueous suspensions. Furthermore, certain steroids which are normal body constituents become carcinogenic when administered in sesame oil. Bishoff, in his review (120), quotes evidence from the literature, according to which sesame oil is placed high on the list of vehicles enhancing the action of carcinogenic hydrocarbons. Bishoff and co-workers (117–119) reported that the cocarcinogenic activity of sesame oil was shown by crude concentrates, but that neither pure sesamin nor sesamol were active. Sesamolin, tested at 90% purity, was similarly found to be inactive. The question of cocarcinogenic activity of sesame oil obviously needs further clarification, but so far there is no evidence that the effect is due to any of the specific constituents of the oil.

The toxicity of sesamol was investigated in rats and rabbits by Ambrose, Cox and DeEds (121). Long-term feeding (up to 1% of diet) to rats caused some proliferative lesions, mostly of a benign character, but did not affect growth, mortality or blood morphology. Tests for skin irritation and sensitization were negative, but intradermal injections caused necrosis in rats. Bishop (120) reported that subcutaneous injection of sesamol in aqueous isotonic solution produced local necrosis in mice.

The growth-inhibiting effect of sesamin and closely related compounds on *Mycobacterium tuberculosis* in vitro was reported from two laboratories (122,123). The antituberculous activity appears to be related to the presence of the methylenedioxy group (123), an observation which calls to mind the synergistic effect of such compounds with pyrethrins.

Chou and Marlatt (124) found that sesame oil produced better carotene utilization than did soybean or peanut oil. This effect may be caused by the liberation of the antioxidant sesamol from sesamolin in the digestive tract. Certain antioxidants are known to increase the utilization of carotene. The possibility that sesamol might act by forming a complex with vitamin A aldehyde (see below) should also be considered.

Ershoff (125) reported that toxicity of fish oils to chicks could be prevented by sesamol. This seemed to be an antioxidant effect since other antioxidants, such as alpha-tocopherol and N,N′-diphenyl-*p*-phenylenediamine (DPPD) similarly counteracted fish oil toxicity.

Stability Questions

Sesamol has been found to form a crystallizable complex with vitamin A aldehyde (126). This complex contains two moles of vitamin A aldehyde per mole sesamol. It is resistant to oxidation but split by alkali. Vitamin A may be formed from it by reduction with borohydrides (127).

According to a recent Indian patent claim (128), sesamin, sesamol, sesamolin and certain other 3,4-methylenedioxyphenyl compounds increase the stability of aqueous physostigmine sulfate solutions. The presence of a phenol group is apparently not a requirement, so that the stabilizing action of these compounds is not due to a simple antioxidant effect.

The comparative antioxidant activity of sesamol and other antioxidants in various fats and oils has been evaluated (129,130). Compared to commercial antioxidants, sesamol is second only to propyl gallate and nordihydroguaiaretic acid in stabilizing lard (129). It should be noted that the usual antioxidants are either polyphenols, or monophenols of the "hindered" type. Sesamol is none of these. To some extent it resembles delta-tocopherol in having unsubstituted alpha carbon atoms and an ether oxygen in para position. Because of its relatively simple structure, sesamol should be a good substrate for investigating antioxidant mechanisms and the relation between structure and activity.

The changes in sesamol and sesamolin during storage of sesame oil have been studied by Oikawa (131) and by Beroza and Kinman (29). The latter authors reported that free sesamol increased somewhat during development of rancidity. This interesting observation seems to prove that some sesamol is liberated from sesamolin during storage. It is difficult, however, to understand why the oil is not stable under these conditions.

The effect of sesame oil on the stability of oils to which it is added is a problem of practical importance because, as mentioned before, regulations in various countries require the addition of sesame oil to margarine or hydrogenated fats, to serve as an indicator. The stability of vitamin A or carotene in such mixtures is equally important. These problems have been investigated principally in India.

Carotene has been reported to be most stable in sesame oil, as compared to other vegetable oils and animal fat (132). Sesame oil added to vanaspati stabilizes the carotene present in direct proportion to the intensity of the Villavecchia test (133). But

opposite results have also been reported. Thus, refined sesame oil has been stated to accelerate the deterioration of vanaspati and of carotene added to it (134). Synthetic vitamin A was reported to be less stable in sesame oil than in other oils and fats (135). The interrelation between color test of sesame oil and vitamin A and oil stability has been studied (136,137), but again the results are contradictory. The stability of vitamin A in sesame oil, margarine stock and a mixture of 5% sesame oil and 95% margarine stock was investigated by Murray et al. (138). These authors found no significant difference in stability of vitamin A in these three fats when stored at 0C. At ordinary temperature, however, the vitamin was less stable in sesame oil. Obviously, the results obtained in such kinds of studies will depend on the type of hydrogenated fat used, on the way the sesame oil has been processed, on the storage conditions, etc. Hydrogenated fats are much more resistant to autoxidation than liquid oils, and vitamin A would also be expected to be more stable in hydrogenated fats than in more unsaturated oils. Refined deodorized sesame oil usually contains only traces of free sesamol and is no more stable than other liquid oils of similar degree of unsaturation. If the oil has undergone sufficient autoxidation, it will act as a pro-oxidant toward vitamin A or carotene, or other fats. On the other hand, under certain processing conditions, free sesamol may be formed from sesamolin, accompanied by a considerable increase in both stability and stabilizing action on other fats or vitamin A or carotene.

In this connection, it must be emphasized again, that the regulations demanding the addition of sesame oil to margarine or hydrogenated fats are antiquated and impose an unnecessary burden on the producer. The adulteration of butter by margarine or the presence in butter fat of hydrogenated vegetable oils can be detected by other more up-to-date techniques, such as IR and UV spectrophotometry and various chromatographic procedures.

ACKNOWLEDGMENT

Information on certain synergists and some recent publications from M. Beroza.

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[Received February 1, 1963—Accepted October 3, 1963]

The Effect of Dietary Fat on the Glyceride Structure of Rat Carcass Fat[1]

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Abstract

Carcass fats were obtained from weanling rats fed a complete diet for 8 weeks, which consisted of 2% cottonseed oil and 10% of the following fats: (1) corn oil; (2) the fatty acids of corn oil; (3) triricinolein; (4) ricinoleic acid; (5) the hydrogenated fatty acids of castor oil; and (6) commercial hydrogenated shortening. The fats were subjected to both pancreatic lipase and nonspecific hydrolysis; the resulting acids converted into methyl esters by conventional methods, and subjected to gas chromatographic analysis. From these data, the positional distribution of the component fatty acids, glyceride types, and isomeric forms were calculated. The results indicated a preferential placement of unsaturated acids in the 2- position of the carcass triglycerides and that the carcass fat composition in terms of unsaturated (U) and saturated (S) fatty acid composition is not greatly influenced by the S and U compositions of the dietary fat. It was found that hydroxy acids or their triesters are metabolized much the same as are normal triglycerides and exert no particular influence upon the fat structure of the rat. Some type of relationship between the dietary U and the U_3 in the carcass fat appears to be present. The glycerides of the carcass fats examined here are essentially a random mixture of the major glyceride types, but the isomeric forms (SUS, SSU, USU and UUS) are a definite non-random mixture.

Introduction

Numerous reports (1,2,3) concerning the effects of dietary fats upon the fatty acid composition of depot fat of animals have recently appeared. It is generally agreed that the fatty acid composition of the depot fat of an animal will reflect the fatty acid composition of the ingested fat. However, few reports concerning the effects of dietary fats upon the triglyceride structure of depot fat have appeared. The glyceride structure of depot fat has been studied by Hilditch (4), Kartha (5) and others. As a result of this work several theories have been proposed to account for the observed differences in depot fat glyceride structure found in various species of animals. These theories have been aptly reviewed by Deuel (6) and VanderWal (7). Reiser et al. (8) have studied, by means of isotope dilution techniques, the glyceride structure of chick and rat fats when the animals were fed fat-free diets. The influence of ingested fat, fed at the 20% level was studied in the same manner. These authors found that the glyceride structure of endogenous rat fat in terms of saturated components (S) and unsaturated components (U) conformed to a random distribution pattern and that ingested fat appeared to be deposited according to the even type of distribution.

Tove et al. (9) recently have shown that the distribution of linoleic acid in depot fat triglycerides of the mouse is apparently dependent on the level of linoleate fed. These authors (10) have also stated that "the effect of increased depot fat levels of linoleate and oleate, and the distribution of other fatty

[1] Carried out at the Food Res. Div., Armour & Co., and at The Burnsides Research Laboratory under research grant No. EF 225 from the National Institutes of Health, U. S. Public Health Service, and Deparmtent of Health, Education, and Welfare.