leucoanthocyanin was obtained as a yellowish powder; yield, 7.8 g.

The reddish brown precipitate obtained by the acetone-benzene method was dissolved in 20 ml. methanol, and, after 2 weeks, 1.7 g. of mumenin was obtained as yellow crystals.

Thus, from 2.1 kg. wood chips of *Prunus mume*, 30 mg. (+)-catechin, 1.0 g. (−)-epicatechin, 32 mg. naringenin, 0.3 g. prunin, 0.2 g. of a new flavanone glycoside, 7.1 g. mumenin, and 7.8 g. leucoanthocyanin were obtained.

(+)-*Catechin*. The melting point of (+)-catechin (97°) as well as of its anhydrous substance did not alter when mixed with authentic specimens obtained from *Prunus yedoensis*.[1]

(−)-*Epicatechin*. After recrystallization from water, it was obtained as plates of m.p. 236°. It gave a green coloration with ferric chloride. The chromatographic data (R_f 0.18 in *m*-cresol: acetic acid: water 25:1:24, R_f 0.52 in isopropyl alcohol: water 22.78) agreed with that of an authentic specimen which was kindly supplied by Prof. Tsujimura.[5] The melting point was not depressed by admixture with the authentic specimen (m.p. 236°). Acetate: m.p. 150°.

Naringenin. After 3 recrystallizations from dilute methanol, naringenin melted at 246°, yield: 32 mg. The mixed melting point with an authentic specimen (m.p. 248°) obtained from *Prunus yedoensis*[1] was the same.

Prunin. This glycoside proved to be identical with authentic prunin (m.p. 224°) on chromatographic comparison and by mixed melting point determination. On hydrolysis with 2% hydrochloric acid, it produced naringenin of m.p. 246° and glucose (ascertained by paper chromatography).

Mumenin. This glycoside showed a greenish brown coloration with ferric chloride and an orange one with magnesium powder and hydrochloric acid in methanol solution. Mumenin crystals are difficultly soluble in most organic solvents except pyridine and dioxane. It was recrystallized from pyridine-water and gave microscopic yellow prisms of m.p. 278°. R_f: 0.95 (*m*-cresol: acetic acid: water 25:1:24), and 0.10 (isopropyl alcohol: water 22:78). Absorption: λ_{max} 260 mμ, 320 mμ, 367 mμ; λ_{min} 239 mμ, 285 mμ, 329 mμ.

Anal. Calcd. for $C_{22}H_{22}O_{11}.{}^1/_2H_2O$: C, 56.05; H, 4.88; OCH_3, 6.58. Found: C, 56.00; H, 4.85; OCH_3, 6.52.

Mumenin pentaacetate. This acetate was prepared by the usual method using acetic anhydride and one drop of conc. sulfuric acid. It was obtained in colorless long prisms of m.p. 210–212°.

Anal. Calcd. for $C_{34}H_{34}O_{17}$: C, 57.14; H, 4.76. Found: C, 56.76; H, 4.92.

Hydrolysis of mumenin. The glycoside (0.1095 g.), 55 ml. water, and 16 ml. conc. sulfuric acid were heated for 8 hr. under refluxing. After cooling, the precipitated aglycone was collected, washed, and dried: yield, 0.0719 g. After the aglycone was filtered, the filtrate was neutralized with barium hydroxide and then barium carbonate. The neutralized solution was dried over potassium hydroxide granules in a vacuum desiccator, and examined chromatographically. Glucose was the only sugar found.

The aglycone (kaempferid) was recrystallized from dilute methanol 3 times and obtained as yellow prisms of m.p. 228°.[6] Absorption: λ_{max} 266 mμ, 367 mμ; λ_{min} 240 mμ, 280 mμ.

Anal. Calcd. for $C_{16}H_{12}O_6$: C, 64.00; H, 4.03. Found: C, 63.88; H, 4.02.

Kaempferid triacetate, m.p. 197°.

Kaempferid trimethyl ether (*kaempferol tetramethyl ether*). This derivative was obtained as faint yellow needles of m.p. 158° by heating an acetone solution of kaempferid with dimethyl sulfate and potassium carbonate. The mixed melting point of kaempferid trimethyl ether with the authentic specimen of kaempferol tetramethyl ether was not depressed.

Anal. Calcd. for $C_{19}H_{18}O_6$: OCH_3, 36.25. Found: OCH_3, 36.51.

Mumenin dimethyl ether. Mumenin (0.4 g.) was suspended in 200 ml. acetone. Then 10 g. potassium carbonate and 2 ml. dimethyl sulfate were added and the whole was heated for 16 hr. When the reaction was over, the liquid was evaporated after removal of mineral salts; the residue was mixed with water; and the solidified mass was washed with water and recrystallized from methanol to produce faint yellow prisms of m.p. 248–250°; yield, 0.2 g. Absorption: λ_{max} 260 mμ, 310 mμ (inflection), 344 mμ; λ_{min} 247 mμ, 283 mμ.

Anal. Calcd. for $C_{22}H_{20}O_9(OCH_3)_2$: OCH_3, 18.97. Found: OCH_3, 19.05.

Hydrolysis of mumenin dimethyl ether. A mixture of mumenin dimethyl ether (125 mg.) and 50 ml. of 4% sulfuric acid was heated over a flame for 40 min. After cooling, the precipitate was filtered and recrystallized from methanol to give yellow needles of m.p. 282°.[7] The yield was 64.5 mg. It gave no coloration with ferric chloride.

Anal. Calcd. for $C_{18}H_{16}O_6$: OCH_3, 28.38. Found: OCH_3, 28.40.

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An Improved Procedure for Preparing Glycerol Ethers[1]

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Batyl alcohol, a natural occurring glycerol ether found in the liver of various Elasmobranchii (shark, rays, etc.) was found to be identical with 1-stearyl glycerol ether.[3–5] The 1- and 2-stearyl

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(2) Portion of a thesis presented by S. C. Gupta as partial fulfillment of the requirements for the degree of Doctor of Philosophy in Food Technology.

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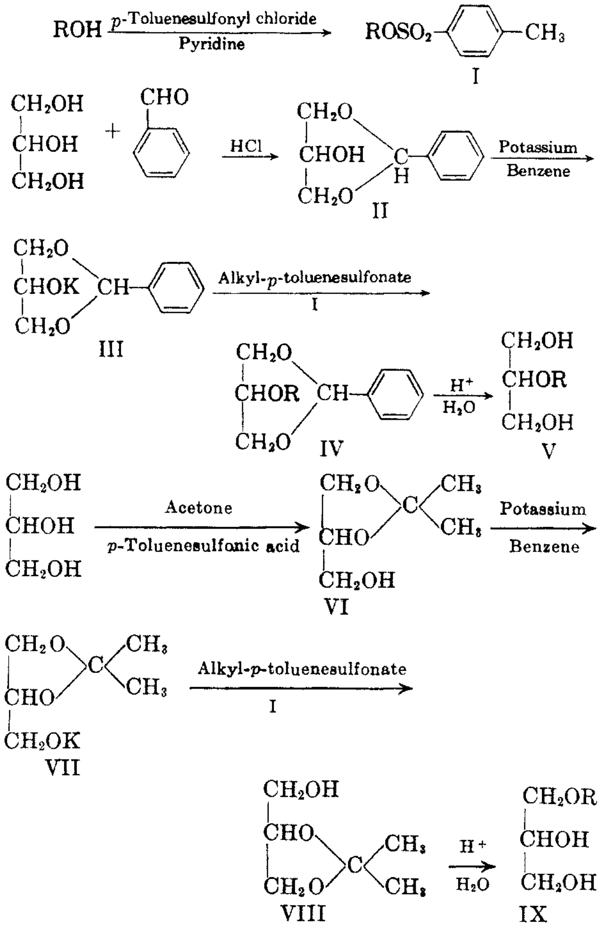
glycerol ethers have been prepared by condensing an excess amount of stearyl iodide with the potassium salt of 1,3-benzylideneglycerol or of 1,2-isopropylideneglycerol in benzene, followed by hydrolysis with acetic acid.[5] The excess stearyl iodide was removed by distillation under vacuum. The unsaturated glycerol ether–selachyl alcohol (1-oleyl glycerol ether) has been prepared in both (+) and (−) forms by condensing oleyl *p*-toluenesulfonate with the sodium salts of (+) and (−)-1,2-isopropylideneglycerol in glycol dimethyl ether.[6] The sodium salts of (+)- and (−)-1,2-isopropylideneglycerol were obtained by using sodium naphthalene as an intermediate compound. Later it was found by the same authors[7] that elaidinization had occurred during synthesis, and they therefore modified their procedure by condensing (+)- and (−)-1,2-isopropylidene-3-(*p*-toluenesulfonoyl) glycerol with sodium oleoxide. The latter was prepared by the use of sodium naphthalene as an intermediate. Baer *et al.*[6] had found that traces of naphthalene were difficult to remove, the products had to be distilled in a molecular still several times before they could be obtained in pure form.

In the present method for the preparation of glycerol ethers, the procedures of Davis *et al.*[5] and that of Baer and Fischer[6] were combined. The stearyl *p*-toluenesulfonate[6] (I) was condensed with the potassium salt of 1,3-benzylideneglycerol (III) or of 1,2-isopropylideneglycerol (VII) in benzene.[5] By this modified procedure, the crude glycerol ethers from stearyl alcohol were obtained in 90–96% yield on the basis of stearyl *p*-toluenesulfonate (I). The intermediate products, 1,3-benzylideneglycerol 2-stearyl ether (IV) as well as 1,2-isopropylideneglycerol 3-stearyl ether (VIII) were isolated in the crude state. It was found from the saponification value of these crude intermediate products that the *p*-toluenesulfonyl group in stearyl *p*-toluenesulfonate (I) was displaced completely. These intermediate products were purified by crystallization from petroleum ether (40–60°), m.p., 59–60°; 60–61°, respectively. On hydrolysis of 1,3-benzylideneglycerol 2-stearyl ether (IV) with dilute hydrochloric acid, 2-stearyl glycerol ether (V) was obtained, m.p. 69–70°. It has been reported to melt at 62–63° by Davis *et al.*[5] The possibility of this compound being 1-stearyl glycerol ether (IX) was eliminated because it could not be oxidized by periodic acid.[8] Moreover, when 2-stearyl glycerol ether (IV) was mixed with an equal quantity of 1-stearyl glycerol ether (IX), the mixture melted at 60–64°.

The syntheses of 2-oleyl and 2-linoleyl glycerol ethers have been attempted by this modified procedure. Analysis of samples by means of infrared spectrophotometer indicated that these glycerol ethers were not elaidinized during their preparation. Due to difficulties encountered in purification, they have not been obtained in pure enough form for accurate carbon hydrogen values.



EXPERIMENTAL

1,3-Benzylideneglycerol (II). The method of Carter *et al.*[9] was used to prepare this compound from glycerol (C.P.) and benzaldehyde. It was obtained in 20% yield, m.p. 81–82°.

1,2-Isopropylideneglycerol (VI). The method described in organic syntheses[10] was used to prepare this compound from glycerol (C.P.) and acetone (C.P.). It was obtained in 87.4% yield, n_D^{25} 1.4388.

Stearyl alcohol. This alcohol was obtained from a sample of commercial alcohol[11] by repeated crystallization from ethyl acetate, m.p. 56°.

Stearyl p-toluenesulfonate (I). The stearyl *p*-toluenesulfonate (I) was prepared by condensing stearyl alcohol with *p*-toluenesulfonyl chloride in the presence of pyridine.[6] It was purified by crystallization from petroleum ether, yield 84.2%, saponification value 131.9 (calcd. 132), and m.p. 56°.

2-Stearyl glycerol ether (V). This ether was prepared in two stages; in the first stage, 1,3-benzylideneglycerol 2-stearyl

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