TABLE II

Effect of Storage Moisture on Chemical Composition of Dixie Runner, Early Runner, and Virginia Runner G-26 Peanut Kernels

Storage time	Kernel moisture % dry wt.	Oil content % dry wt.	Peroxide value	Carbonyl compounds mM/kg.-oil	F.F.A. as % T.F.A.	Iodine value	Tocopherols mg./g.	Total nitrogen % kernel dry wt.	Protein nitrogen % kernel dry wt.	Total sugars mg./g.
Dixie Runner										
None	7.0	47.6	1.5	0.45	0.22	91.2	0.10	4.4	3.8	27.5
3½ months	4.8	47.7	1.5	0.52	0.22	91.7	0.10	4.4	3.8	27.5
3½ months	5.4	47.7	2.0	0.55	0.22	91.5	0.10	4.4	3.7	27.4
3½ months	6.7	47.4	2.2	0.72	0.25	92.0	0.09	4.2	3.7	28.4
3½ months	7.7	47.9	2.0	0.92	0.40	91.7	0.12	4.4	3.8	28.0
3½ months	10.6*	47.9	4.2	1.00	1.47	91.6	0.17	3.9	3.8	26.4
Early Runner										
None	7.6	52.5	1.0	0.65	0.22	90.7	0.12	4.3	3.8	23.3
3½ months	5.1	52.6	2.5	0.54	0.22	91.0	0.12	4.2	3.8	23.3
3½ months	6.4	52.1	2.5	0.49	0.22	91.5	0.13	4.3	4.0	23.0
3½ months	8.0	52.5	2.3	0.65	0.22	91.0	0.12	4.2	3.7	23.2
3½ months	8.7	52.4	2.5	0.44	0.47	91.0	0.10	4.3	3.9	22.7
3½ months	10.0*	51.3	5.2	0.56	7.60	91.5	0.13	4.3	3.8	23.2
Virginia Runner G-26										
None	7.8	48.6	1.0	0.65	0.40	91.0	0.13	4.1	3.7	28.8
3½ months	5.1	48.6	1.0	0.44	0.40	91.0	0.13	3.9	3.8	28.5
3½ months	6.6	48.2	1.0	0.41	0.40	91.0	0.12	3.9	3.7	28.5
3½ months	7.7	48.6	1.0	0.66	0.38	90.5	0.13	4.2	3.9	29.3
3½ months	8.6	48.5	1.0	0.55	0.40	91.5	0.13	4.1	3.7	29.3
3½ months	11.2*	48.4	2.0	0.63	9.15	91.0	0.15	4.1	3.7	28.6

* Fungus growth was observed at these moisture levels.

Dixie variety (at 10.6% moisture) was thought to be due to the growth of seed storage fungi on these samples. Ward and Diener have reported on changes in stored peanuts caused by fungi (10).

Other differences noted were palatability and germinability. Dixie and Early were rated equal in palatability. G-26 was consistently rated the best-tasting by a taste-test panel. Dixie and Early germinated readily after curing, germinability being greater than 70%. G-26 gave only 10% germination immediately after curing, and required a rest period of several weeks before germinability reached 70%.

Differences in the three varieties in chemical composition, and stability during storage, were not great enough to be used as criteria for variety recommendations. However, differences did exist in oil content, sugar content, taste, germinability, and susceptibility to rancidity development during storage.

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The Preparation and Properties of Polyoxyethylene Methyl Glucoside Fatty Esters[1]

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New, nonionic, emulsifying agents, the polyoxyethylated methyl glucoside esters of some saturated and unsaturated fatty acids, are described. One series, Type A, was prepared by etherification of the glucoside esters. In another, Type B, the ethers of methyl glucoside were esterified.

In general, the esters exhibit good emulsifying action; the unsaturated esters, particularly Type B, also possess film-forming properties. Such compounds may have value in preparing emulsion paints. The surface tension of water is appreciably lowered by adding as little as 0.01% of the polyoxyethylene methyl glucoside esters.

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[2] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

GIBBONS AND SWANSON prepared methyl glucoside fatty esters by direct esterification and investigated the surface-active properties of several of the diesters (1,2). In general the methyl glucoside diesters of highly saturated fatty acids do not disperse in water. Reaction of ethylene oxide with fatty esters of sorbitan (3,4) and of sucrose (5) has produced polyoxyethylene ethers with enhanced water solubility and has extended applications of these carbohydrate derived products as emulsifying agents. It was therefore of interest to prepare polyethers of a number of fatty esters of methyl glucoside by reaction with ethylene oxide, and to investigate their surfactant behavior.

TABLE I

Preparation and Properties of Methyl Glucoside Esters

Type	Charge, moles		Cooking schedule		Acid No.	Saponication No.		Physical appearance
	Fatty acid	Methyl glucoside	°C	Hr		Exptl.	Theory	
Products with high monoester content[a]								
Stearate	0.3	0.3	175	3.75	12	128	122	White solid[b]
Linoleate	0.3	0.3	175	3.5	5	132	123	Orange wax[b]
Oleate	0.3	0.3	175	3.75	4	126	122	Orange wax[c]
Laurate	0.4[d]	0.4	175	5.0	11	154	149	White wax[b]
Products with high diester content[e]								
Stearate	0.2	0.1	180	9.0	4	156	154	Tan solid[c]
Palmitate	0.2	0.1	180	9.0	12	152	167	Tan solid[c]
Linolenate	0.2	0.1	180	8.0	3	160	157	Orange liquid[c]
Oleate	0.25	0.125	180	8.0	5	160	155	Orange, very viscous[b]
Linseedate	0.16	0.08	190	8.0	5	162	156	Amber liquid[c]
Linoleate	0.14	0.07	190	7.0	4	159	156	Yellow, highly viscous[c]

[a] Stannous oxide catalyst (0.8% based on fatty acids).
[b] Bleached with hydrogen peroxide.
[c] Treated with Darco G-60 at end of reaction.
[d] Stannous oleate catalyst (3% based on fatty acid).
[e] Litharge catalyst (0.35% based on fatty acid).

This paper is a preliminary report on the ethylene oxide reaction products of methyl glucoside fatty esters. One series (Type A) was made by etherification of the esters with approximately 5-, 10-, 15-, and 20-mole equivalents of ethylene oxide. Methyl glucoside esters containing a high monoester content were prepared by direct reaction with stearic and lauric acids following Gibbons' method and were readily etherified. Several unsaturated monoesters were also prepared by this procedure, but the trace of stannous salt catalyst adversely affected any subsequent ethylene oxide reaction, and the products were not investigated further. Diesters of methyl glucoside synthesized by reaction with stearic, palmitic, linoleic, linolenic, and linseed oils acids were etherified with ethylene oxide with no difficulty. Another series of products, Type B, was prepared by esterification of various polyoxyethylene methyl glucosides with most of the fatty acids described. Purification of the products was not attempted and the terms mono- and di- refer only to average ester content rather than to homogeneous substances.

Ethylene Oxide Reaction Products of Methyl Glucoside Esters (Type A)

Monoesters. Esters of more than 70% monoester content were prepared as described by Gibbons (1,6). The following preparation of monostearoyl methyl glucoside illustrates the procedure:

Stearic acid, 85.4 g (0.3 mole), was heated under a blanket of carbon dioxide to 180°C in a flask equipped with a magnetic stirrer, thermometer, gas inlet tube, and condenser. Stannous oxide, 0.68 g, was added and the temperature raised to 235°C until the solution was light in color (20–25 min). The system was cooled to 180°C, then charged with 58.2 g (0.3 mole) of methyl glucoside, the temperature was maintained at 175°C with rapid carbon dioxide sparge and with good agitation until the acid number was below 8 (3.75 hr). The dark-colored solution was cooled to 90°C and bleached cautiously by stirring with 4.3 ml of 50% hydrogen peroxide until the product was nearly colorless (30–60 min). Increasing the temperature to 110°C removed the water. The product was filtered, dissolved in ethanol, and refiltered three times through fine paper. Solvent was removed *in vacuo*.

Diesters. Products of high diester content were prepared by the direct esterification of methyl glucoside with fatty acids using litharge catalyst and the solvent method of Gibbons and Swanson (1).

Preparation and Properties. Reaction conditions and some chemical and physical properties of the methyl glucoside esters are listed in Table I.

Etherification with Ethylene Oxide. Esters were heated to 160°C in a 250-ml three-necked flask fitted with a nitrogen sparge tube, magnetic stirrer, thermometer, and an outlet tube (7,8). Sodium methylate or sodium hydroxide (0.2–0.5%) was added and the nitrogen sparge replaced with ethylene oxide.

TABLE II

Properties of Type A Polyoxyethylene Methyl Glucoside Esters

Product	C_2H_4O[a] groups per mole	Saponification value	Color[b]	Viscosity[b]	Solubility[c] in water at 25°		Surface tension dynes/cm at 25° % conc. in water			Emulsion stability (time in min. for H_2O separation)	
					1%	0.1%	1%	0.1%	0.01%	10 ml	20 ml.
Monolaurate	5	96	14	Y	2	3	31	33	36	15	30
Monolaurate	10	74	17	U	3	3	32	32	38	25	53
Monolaurate	15	61	17	R	3	3	34	34	37	27	56
Monolaurate	20	49	15	R	3	3	34	34	36	26	56
Monostearate	5	85	Brown	Wax	2	2	39	41	54	1	....
Monostearate	10	68	Brown	Wax	2	3	38	39	37	20	....
Monostearate	15	53	Brown	Wax	3	3	40	40	43	25	....
Monostearate	19	....	Brown	Wax	3	3	40	40	41	22	....
Dilinseedate	20	72	18	P	3	3	40	40	41	18	41
Dilinoleate	19	62	14	R	3	3	40	41	43	16	34
Dioleate	5	124	17	T	1	2	30	33	42	1	2
Dioleate	11	96	18	P	2	2	34	36	40	6	10
Dioleate	15	83	18	P	2	3	37	34	36	10	....
Dioleate	24	70	18	L	3	3	39	39	39	17	35
Distearate	29	55	Tan	Wax	3	3	43	43	44	16	35
Dipalmitate	22	65	12	Q	1	3	40	39	41	22	48
Dilinolenate	19	74	14	R	2	3	37	39	40	13	27

[a] Number of C_2H_4O groups per mole based on increase in weight.
[b] Gardner (1933) color; Gardner Bubble Viscometer.
[c] Solubility code: 1 = milky dispersion after vigorous agitation; 2 = stable milky dispersion; 3 = clear solution.

TABLE III

Properties of Type B Polyoxyethylene Methyl Glucoside Esters

Product	C_2H_4O[a] groups per mole	Saponification value	Color[b]	Viscosity[b]	Solubility[c] in water at 25°		Surface tension dynes/cm at 25° % conc. in water			Emulsion stability (time in min. for H_2O separation)	
					1%	0.1%	1%	0.1%	0.01%	10 ml	20 ml
Monolinseedate	15	50	11	S	3	3	38	42	43	19	38
Dilinseedate	15	85	12	J	2	2	40	43	45	16	33
Distearate	20	73	Tan	Wax	Insoluble	Insoluble	....	....	....	12	26
Dipalmitate	20	72	10	S	1	2	41	41	42	26	53
Dilinolenate	20	71	11	L	3	2	37	40	44	25	46
Dilinolenate	5	125	14	M	1	2	32	38	39	3	7
Dilinolenate	10	99	13	K	1	2	35	43	48	4	8
Trilinseedate	15	109	14	J	1	2	35	50	52	2	4
Dilinseedate	5	117	14	R	1	1	....	39	41	1	2
Dilinseedate	10	97	14	O	1	2	....	40	42	7	14

[a] Number of C_2H_4O groups per mole based on increase in weight.
[b] Gardner (1933) color; Gardner Bubble Viscometer.
[c] Solubility code: 1 = milky dispersion after vigorous agitation; 2 = stable milky dispersion; 3 = clear solution.

Temperature was maintained at 160–175°C (180–190°C greatly increased the reaction rate), and samples were removed at various levels of etherification as indicated by weight increases. The monoesters required about 10-mole equivalents and the diesters about 15– to 20-mole equivalents of ethylene oxide to become water-soluble. The polyoxyethylene esters and their properties are listed in Table II.

Fig. 1 illustrates the rate at which ethylene oxide reacted with 60-g samples of the esters. Samples (30 g) were withdrawn at approximately 5-, 10-, 15-, and 20-mole equivalent levels of reaction of ethylene oxide with esters for physical property measurements.

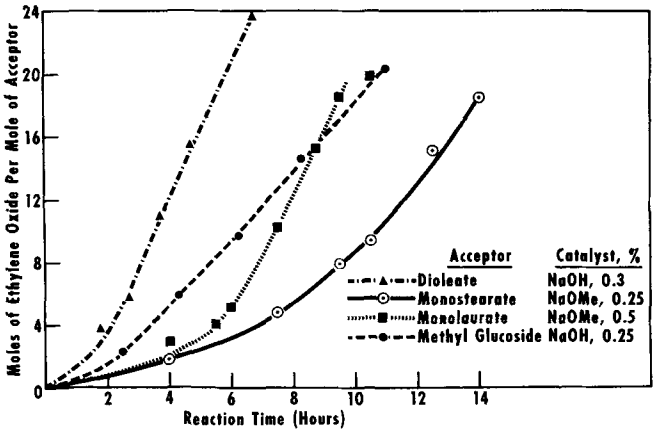

FIG. 1. Rate of ethylene oxide addition to methyl glucoside esters and to methyl glucoside at 170–175°C.

Esters of Polyoxyethylene Methyl Glucosides (Type B)

Polyoxyethylene Methyl Glucoside. Methyl glucoside was reacted with ethylene oxide by the procedure used for the etherification of the esters. Rate of reaction is shown in Fig. 1. The products were amber colored and had viscosities of 21,000 cp (5-mole equivalents of ethylene oxide) to 800 cp (20-mole equivalents of ethylene oxide).

Esterification. The procedure was essentially the same as that described for the preparation of methyl glucoside esters (1). As an example, 27.8 g (0.1 mole) of linolenic acid, 21 g (0.05 mole) of pentaoxyethylene methyl glucoside, 0.1 g of sodium hydroxide (or litharge) and 50 ml of xylene were mixed in a 250-ml three-necked flask fitted with a gas disperser inlet, thermometer, stirrer, and a Dean-Stark trap with condenser. While being stirred under a blanket of nitrogen the contents were heated rapidly to 180°C with sufficient xylene being removed through the trap to maintain reflux at this temperature. Samples were removed at various intervals and titrated to determine the remaining free acid content. After 5 and 9 hr. of reaction, the acid numbers were 14 and 5, respectively. Traces of xylene were removed from the reaction product by increasing the rate of nitrogen sparge.

When litharge was used as catalyst, it was removed from the product by the addition of adipic acid which formed a precipitate of lead adipate that could be separated by filtration. Treatment of several products with activated carbon did not reduce the color appreciably. Although bleaching with aqueous hydrogen peroxide gave light-colored products, properties reported are those obtained prior to bleaching. The esterified polyoxyethylene methyl glucosides and their properties are listed in Table III.

Physical Characteristics of the Esters

Emulsifying Properties. Forty ml. of 0.1% aqueous solution of the surfactant were mixed with 40 ml of light paraffin oil, N.F. in a 500-ml glass stoppered Erlenmeyer flask and manually shaken in five cycles. Each cycle consisted of five violent downward motions and 1 min of standing. The emulsion was then poured into a 100-ml graduate cylinder and the time required for 10 and 20 ml of the aqueous phase to separate was recorded (8). A clear line of distinction between the aqueous and emulsion layers was not obtained with the better emulsifiers. However the emulsion stability values given in Tables II and III are believed to have relative significance. For comparison several commercial nonionic surfactants were also evaluated and found to require a maximum of 18 min for the first 10 ml of aqueous phase to separate. Thus many of these polyoxyethylene methyl glucoside esters of both types appear to have excellent emulsifying properties according to this evaluation method.

Drying Properties. The esters of unsaturated fatty acids were mixed with a small amount of drier consisting of lead and cobalt naphthanates and then cast on glass plates to produce films about 0.004-in. thickness after drying at room temperature. Esters which had been reacted with sufficient ethylene oxide to produce water-solubility formed poor films. The dilinolenate prepared by esterification of the reaction product of ethylene oxide and methyl glucoside (Type

B) in the mole ratio of 20 to 1 formed wrinkled films comparable to nonheat-treated linseed oil.

In contrast, the dilinolenate ester (Type B) prepared from polyoxyethylene methyl glucoside containing five ethylene oxide groups per mole produced a clear and coherent film that was essentially tack-free after 12 hr. Type B dilinseedate esters in which methyl glucoside was first etherified with 5- and 10-mole equivalents of ethylene oxide also showed good film-forming properties, but the films remained tacky. Type A dilinolenate ester containing 19 moles of ethylene oxide per mole of product produced a grainy film. Methyl glucoside esters such as these, which have water dispersibility and yet retain some drying oil properties, could conceivably be valuable for making emulsion paints in that the emulsifying agent would become a part of the paint film (9).

Surface Tension. Surface-tension measurements were made with the Du Noüy tensiometer. The results of these measurements show that the surface tension of water is appreciably lowered by the addition of as little as 0.01% of the polyoxyethylene methyl glucoside esters. The values are comparable to those reported for the methyl glucoside diesters (1) and for polyoxyethylene sorbitan monoesters (5).

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Chemical and Physical Characteristics and Possible Configuration of Toxins from Tung Kernels

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Based on limited chemical and physical data, including the infrared and ultraviolet spectra of the toxins and their saponification products, it is suggested that Tung Toxin I and Tung Toxin II are diesters of a 2,3-unsaturated-5-keto acid, a polyhydroxy acid and a 3,4-unsaturated-5-keto tertiary alcohol. The 2,3-unsaturated-5-keto acid is assumed to be in equilibrium with its enol tautomer, the keto form possessing a conjugated diene and the enol form a conjugated triene structure. The polyhydroxy acid is probably very similar to gluconic acid.

THE LITERATURE on the toxicity of tung meal has been reviewed by Mann, Hoffman and Ambrose (6) and by Balthrop, Gallagher, McDonald and Camariotes (1). More recently Holmes and Rayner (5) described a procedure for isolating two nitrogen-free toxins, designated as Toxin I and Toxin II, from oil-free kernels, and reported certain of the characteristics of the toxins. They found Toxins I and II to have the empirical formulas $C_9H_{14}O_2$ and $C_{11}H_{16}O_3$, respectively. Both toxins were optically active. Toxin I contained 5.7% hydroxyl and had a saponification equivalent of 268. Toxin II contained 5.6% hydroxyl and had a saponification equivalent of 401.

This paper reports additional characteristics of the toxins.

Experimental

Small amounts of Toxins I and II were isolated from tung kernels using the procedure developed by Holmes and Rayner (5). These gave single spots in glass paper chromatography with the same Rf values as the toxins reported in the previous paper.

Numerous qualitative tests were applied to the toxins but few were found to be positive. The molecular weights (7), hydrogen iodine values (8), and optical activities of the toxins were also determined by established procedures.

Two samples of each toxin were saponified, one under mild conditions by allowing sample to stand overnight at room temperature in absolute ethanol adjusted to about pH 11 with KOH, the other by refluxing the sample with alcoholic KOH (40 g./l. in 95% ethanol) for 1.5 hrs. The saponified samples were separated into three fractions; the ethyl ether extract of an aqueous alkaline solution referred to as the "unsaponifiables," the acids extracted by ethyl ether after acidification of the solution with hydrochloric acid, and the residue that remained in the water solution. In none of the fractions of the saponified samples could the spots characteristic of Toxins I and II in glass paper chromatography be detected. This was taken as evidence that saponification was complete.

Ultraviolet spectra of the toxins and their saponification products were obtained from 99% ethanol solutions over the region 220 to 360 mμ with a Cary Automatic Recording Spectrophotometer Model 14. The instrument was first balanced throughout this range with the solvent in two matched 2-cm. path-length cells.