35.0 g. (0.26 mole) of aluminum chloride was heated at 80° for one hour after the exothermic reaction had ceased. The reaction product, which was worked up in the same way, consisted of colorless prisms, m.p. 207–208° (from benzene), yield 89%.

Anal. Calcd. for $C_{16}H_{10}Cl_6O_3$: C, 41.47; H, 2.16; neut. equiv., 463. Found: C, 41.75; H, 2.24; neut. equiv., 462.

Ethyl ester: colorless platelets from aqueous ethanol, m.p. 113–114°.

Anal. Calcd. for $C_{18}H_{14}Cl_6O_3$: C, 44.02; H, 2.87. Found: C, 44.19; H, 2.75.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]5-heptene-2,3-dicarboximide.—An excess of concentrated ammonia was slowly added with stirring to 17.1 g. (0.1 mole) of powdered chlorendic anhydride. A vigorous exothermic reaction occurred when the reactants were mixed. The mixture was allowed to stand overnight, 200 ml. of water was added and a small amount of unchanged acid removed by filtration. The filtrate was acidified with sulfuric acid and the precipitated imide was filtered with suction and crystallized from aqueous ethanol, colorless plates, m.p. 279–280°, yield 95%.

Anal. Calcd. for $C_{15}H_8Cl_6NO_3$: C, 29.19; H, 0.81; N, 3.78. Found: C, 29.12; H, 1.04; N, 3.85.

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Photoinitiated Diradical Polymerization of Methyl Methacrylate

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Benzoin has been known for some years to be an effective photoinitiator for vinyl polymerization,[1] but the mechanism has remained unknown. It has been shown that although simple ethers of benzoin are effective photoinitiators,[2] oximes, in which the carbonyl function is changed, are generally ineffective. This evidence supports a hypothesis that the carbonyl group is the active group of benzoin and that modifications involving the hydroxyl do not change the activity significantly. To obtain information about how the benzoin derivatives are combined in the polymer resulting from photoinitiated polymerization, carbon-14 tagged benzoin methyl ether was used for a study of the photopolymerization of methyl methacrylate. Methyl methacrylate was selected as a subject monomer because the amount of chain transfer involved is lower than with many other monomers.[3]

Polymer prepared by photoinitiation with benzoin methyl ether tagged with carbon-14 in the methyl group was washed to free it of uncombined initiator and its molecular weight determined by viscosity measurements in benzene. The viscosity–molecular weight relationship of Baxendale, Bywater and Evans,[4] was used to calculate molecular weight of the polymer. It is recognized that the molecular weight obtained by this means is a viscosity average, but the final conclusions are not altered significantly by use of calculated number average molecular weights (assuming $\bar{M}_n = 0.7\,\bar{M}_v$).

The radioactivity of the polymer after precipitation two and three times was determined by combustion and count in an internal gas-flow type counter. The figures obtained after successive precipitations indicated that uncombined benzoin methyl ether had been removed. The effectiveness of reprecipitation for removal of benzoin methyl ether was further checked by examination of polymethyl methacrylate made by a thermally-initiated polymerization in the presence of tagged benzoin methyl ether. Such polymer after two precipitations did not retain significant activity, indicating that the uncombined benzoin methyl ether was removed readily by the precipitation technique used and that there was no significant amount of free radical chain transfer with the benzoin methyl ether, which would have resulted in its combination in the polymer.

Three polymerizations using different amounts of benzoin methyl ether produced polymers containing an average of 12.3 to 14.7 benzoin methyl ether residues per polymer molecule (see Table I). These are average values; no corrections were made for thermal polymerization of the monomer and the molecular weight distribution of the polymer was not measured.

TABLE I

PHOTOINITIATION WITH LABELED BENZOIN METHYL ETHER

No.	MMA, g.	BME,[a] g.	Time, min.	Polymer, g.	Radioassay,[b] % BME	$[\eta]^c$	$\bar{M}v^d$	BME/polymer mol.
1	7.70	0.0098	20	0.1248	1.10	0.92	252,000	12.3
2	7.68	.0201	30	.2645	1.41	.81	213,000	13.2
3	7.83	.0298	30	.2475	1.53	.82	218,000	14.7

[a] Labeled benzoin methyl ether. [b] BME retained in polymer after third reprecipitation. [c] Mean of $(\ln \eta_{rel})/c$ and η_{sp}/c in benzene at $c = 0.1$ g./100 ml. [d] From $M = 2.81 \times 10^5 [\eta]^{1.32}$.

Although the values for molecular weight are not precisely correct, the values obtained show that there are several initiator fragments combined per polymer molecule on the average. This result may be interpreted either by means of a polymerization mechanism involving diradical initiation and termination by mutual combination or by copolymerization of methyl methacrylate with light-activated benzoin methyl ether. Neither interpretation is entirely satisfactory. The measured molecular weights appear to agree within experimental error with values calculated from reported rate constants and monoradical initiation.[3,5] Furthermore, there appears to be a square-root dependence of the polymerization rate on concentration of the benzoin methyl ether.

Benzoin, a photoinitiator similar to benzoin methyl ether, shows a relatively long-lived low-temperature phosphorescence (half-life 0.024 sec.)[6] indicative of triplet state diradicals.[7] Quantum

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(1) C. L. Agre, U. S. Patent 2,367,661 (January 23, 1945).

(2) M. M. Renfrew, U. S. Patent 2,448,828 (September 7, 1948).

(3) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71**, 497 (1949).

(4) J. H. Baxendale, S. Bywater and M. G. Evans, *J. Polymer Sci.*, **1**, 237 (1946).

(5) B. R. Chinmayanadam and H. W. Melville, *Trans. Faraday Soc.*, **50**, 73 (1954).

(6) Unpublished measurement of Dr. J. C. Rowell of this Laboratory.

(7) G. N. Lewis and M. Kasha, THIS JOURNAL, **66**, 2100 (1944).

yield measurements have shown that 1250 molecules of methyl methacrylate are polymerized per quantum of 3660 Å. radiation in the presence of benzoin. Since benzoin methyl ether appears to be at least equally efficient, this yield appears too high to be consistent with a mechanism involving copolymerization of light-activated benzoin molecules with methyl methacrylate.

Experimental

Preparation of Labeled Benzoin Methyl Ether.—Carbon-14 labeled benzoin methyl ether was prepared from benzoin, carbon-14 labeled methyl iodide and silver oxide by a modification of the method of Wren.[8] The labeled methyl iodide (1 mc. in 1 mm.) was supplied by Tracerlab, Inc., under allocation from the Atomic Energy Commission. The product was recrystallized from petroleum ether.

Polymerization.—Polymerizations were carried out in small tubes of 10-mm. Pyrex brand glass into which freshly distilled methyl methacrylate monomer and labeled benzoin methyl ether were charged as listed in Table I. The tubes were flushed with oxygen-free nitrogen through a long capillary, frozen in Dry Ice–acetone and sealed off under vacuum. They were then brought to room temperature and placed under a reflector holding two BL-360 fluorescent tubes. After polymerization the polymers were precipitated from excess monomer with methanol, dissolved in benzene, and reprecipitated twice. After drying to constant weight, the radioactivity of the polymers was measured by combustion, precipitation as barium carbonate and radioassay in an internal counter. The original tagged benzoin methyl ether was run as a control. The polymers were dissolved and reprecipitated a third time without producing a significant change in activity.

A polymer sample was prepared in the dark by thermal initiation of methyl methacrylate containing benzoin methyl ether and α,α'-azobisisobutyronitrile to determine if exchange or transfer reactions might lead to radioactive products. A 10-mm. Pyrex tube was charged with 7.116 g. of freshly distilled methyl methacrylate, 0.0953 g. of α,α'-azobisisobutyronitrile, and 0.0206 g. of the labeled benzoin methyl ether. This was heated at 50° for 40 minutes in the dark and the polymer recovered as described for the photopolymerizations. Conversion was 9%. The polymer showed no significant radioactivity after two precipitations.

Molecular Weight.—Dry polymers were dissolved in thiophene-free benzene to produce solutions of about 0.1 g. per 100 ml., whose viscosities were measured in Ostwald viscometers. The true intrinsic viscosities were not measured but were estimated from $(\ln \eta_{\mathrm{rel}})/c$ and from $\eta_{\mathrm{sp}}/c = [\eta] + k' [\eta]c$, assuming k' to be 0.4, and viscosity average molecular weights were calculated from the equations of Baxendale and co-workers.[4]

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[8] H. Wren, *J. Chem. Soc.*, **95**, 1585 (1909).

CONTRIBUTION NO. 346
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The Distribution of Triterpenes in Plants.
Chenopodium album

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In a previous communication[2] we noted the accumulation of the pentacyclic triterpene oleanolic acid in mature *Plantago major*. None was found in young plants. Djerassi, *et al.*,[3] have listed the known sources of this acid. We wish to report the presence of oleanolic acid in *Chenopodium album*, or Lamb's Quarters.[4] In this plant it accumulates in the mature growth also but its occurrence is limited to the flower parts only. The acid is not present in any part of the young plants selected for examination before the appearance of the flowers. The non-saponifiable portion of alcoholic extracts of the young and mature plant, respectively, contains sitosterol as the sitosterol mixture.

Of a large number of local plants examined for the presence of both the carboxylated pentacyclic triterpenes and sterols (to be published), only *Chenopodium album* and *Plantago major* were found to contain them together.

Experimental[5]

Isolation of Oleanolic Acid as the Acetate.—Finely ground dried flower parts (1362 g.) of Lamb's Quarters (*Chenopodium album*) were exhaustively extracted with hot, 95% ethanol. The extract was distilled to low volume, made approximately 2 *N* with concd. HCl and refluxed for 2 hr. The cooled solution was diluted with water and extracted thoroughly with ethyl ether. The latter was washed with water, then extracted thoroughly with 5% $NaHCO_3$ (extracts discarded) and 5% KOH, respectively. The ether was then washed with water and distilled, leaving 44.0 g. of neutral, greenish-black wax (see below). The KOH extracts were acidified (HCl) and filtered. The precipitate was washed and dried leaving 8.5 g. of greenish lumps. This crude product was too contaminated with black gum to obtain any crystalline material from it by direct crystallization or crystallization after acetylation with acetic anhydride and pyridine (room temperature). The acetylated mixture was transferred to a 100-g. alumina column with the aid of a little benzene. The column was washed with low boiling (b.p. 30–60°) petroleum ether and 1% ethanol in petroleum ether, respectively (elutes discarded). Washing with 2% ethanol in petroleum ether eluted 1.5 g. of tan needles, m.p. 245–255°. After several crystallizations from methanol and aqueous acetone feathery needles were obtained, m.p. 268–270° undepressed on admixture with authentic oleanolic acid acetate; $[\alpha]^{27}\mathrm{D}$ +75° ($CHCl_3$).[6]

Anal. Calcd. for $C_{32}H_{50}O_4$: C, 77.06; H, 10.10. Found: C, 77.14, 76.98; H, 9.92, 9.89.

Oleanolic Acid.—Microscopic needles, m.p. 308–310°, undepressed on admixture with authentic oleanolic acid; $[\alpha]^{27}\mathrm{D}$ +78° ($CHCl_3$).

Anal. Calcd. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.58. Found: C, 78.63, 78.67; H, 10.43, 10.32.

Acetyl Methyl Oleanolate.—Glistening scales, m.p. 224–225°, undepressed on admixture with authentic acetyl methyl oleanolate; $[\alpha]^{27}\mathrm{D}$ +60° ($CHCl_3$).

Examination of Mature Plant Parts, Other Than Flowers, and Young Lamb's Quarters.—Mature plant parts, other than flowers, did not contain any oleanolic acid, nor did any part of the young plant, selected before the appearance of the flower parts.

Isolation of Sitosterol.—The neutral fractions from the flower parts and whole young plants, after saponification and chromotography, yielded sitosterol as white flakes, m.p. 137–139°, undepressed on admixture with authentic sitosterol mixture. An acetate was prepared, m.p. 125–127°, undepressed on admixture with authentic sitosterol (mixture) acetate.

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[1] Central Research Department, Anheuser-Busch, Inc., St. Louis, Missouri. Address communications to this author.

[2] R. Hiltibran, C. Wadkins and H. Nicholas, THIS JOURNAL, **75**, 5125 (1953).

[3] C. Djerassi, L. Geller and A. Lemin, *ibid.*, **75**, 2254 (1953).

[4] A prolific weed occurring widespread throughout the United States (J. M. Fogg, Jr., "Weeds of Lawn and Garden," Univ. of Penn. Press, Philadelphia, Pa., 1945, p. 73).

[5] All melting points are uncorrected and were determined on the Fisher–Johns apparatus, with the exception of that of oleanolic acid which was determined by the capillary tube method.

[6] Djerassi, *et al.*,[3] give the following constants: oleanolic acid, m.p. 308–310°; acetyl oleanolate, m.p. 264–267°, $[\alpha]^{22}\mathrm{D}$ +70°; acetyl methyl oleanolate, m.p. 217–219°, $[\alpha]^{22}\mathrm{D}$ +65°.